E. Hilsenrath 622

Final Report

for

IITRI Project No. C-6137

(January 5, 1968 to January 5, 1969)

Contract No.: NAS5-11501

Prepared by

IIT RESEARCH INSTITUTE
10 West 35th Street
Chicago, Illinois 60616

for

Goddard Space Flight Center

Greenbelt, Maryland

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Contracting Officer: S. Provenzano
Technical Monitor: E. Hilsenrath

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Project Manager: E. L. Grove

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FOREWORD

The research program entitled "Investigation of Hollow Cathode Excitation Source for Water Vapor Measurements," IITRI Project No. C-6137, was authorized under Contract No. NAS5-11501, Goddard Space Flight Center, Greenbelt, Maryland.

The work described in this report was performed during the period of January 5, 1968 to January 5, 1969.

Personnel who contributed to the project were G. L. Johnson, J. Y. Reich, and Dr. E. L. Grove

ABSTRACT

INVESTIGATION OF HOLLOW CATHODE EXCITATION SOURCE FOR WATER VAPOR MEASUREMENTS

The lack of instrumentation capable of measuring water vapor concentration accurately at altitudes between 25 km and 70 km prompted the research contained in this report. From previous work performed at IITRI, it was known that the emission of light at 6562.8 Å was particularly efficient from the hollow cathode excitation of hydrogen. A program was thus initiated to find a cathode geometry which emitted light of this wavelength over a two magnitude pressure range, and to study the effects of various parameters such as flow rate, current, pressure, etc. on the output at this wavelength with regard to hydrogen concentration in air.

A geometry which fulfills the changing pressure requirements was found. Spectral examination of the discharge, however, showed relatively weak and poorly defined band structures in this region. No record of these structures have been found in the literature. These were associated with nitrogen. One structure was coincident with the 6562.8-Å hydrogen line. This background emission made it difficult to determine the efficiency of the cathode in the ppm range of hydrogen concentration. If another portion of the nitrogen spectrum had been found which varied proportionately with the intensity of nitrogen emissions and/or with the intensity of the 6562.8-Å hydrogen line as the pressure changed the above could have been accomplished.

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INVESTIGATION OF HOLLOW CATHODE EXCITATION SOURCE FOR WATER VAPOR MEASUREMENTS

I. INTRODUCTION

One objective of this program was to lay the groundwork for a flyable instrument and/or a calibration instrument for measuring the water vapor concentration at altitudes between 25 and 70 km using a hollow cathode excitation source and spectrophotometric detection. Specifically, the program was designed as follows:

(A) To determine dependence of light output of the hollow cathode on total pressure, water vapor partial pressure, flow rate, and electrical power input, including determination of the lower pressure limits.

(B) To calibrate the optics and sensor system in order to express the dependencies in absolute light output.

(C) To make a brief study and recommendation on instrument configuration, means of spectral-isolation of emission, and power required.

(D) To devise a technique for removal of interfering gases at representative partial pressures for altitudes above 25 km.

The study described in part (A) of the above was carried out by experimentation using various cathode geometries, gathering data on the effects of the above parameters, and evaluating the geometry from the standpoint of pressure range and hydrogen/nitrogen excitation.

A cathode geometry was found which produces ample light output over the pressure range of 0.1-10 Torr. The excitation characteristics of this geometry were studied carefully. It was found that the underlying nitrogen spectrum contributes significantly to the total light emitted at 6562.8 Å when hydrogen is present in trace quantities. Due to time limitations, a nearby line or band structure with the same excitation characteristics was not found. Since the background due to this nitrogen structure may be subtracted from the total output to give the output due to hydrogen, it was necessary to find such a line or band structure before definitive results may be expected in the ppm hydrogen concentration range.

Calibration in terms of absolute output was performed. However, since time and spectral interferences did not make it possible to accomplish part (A), it was not practical to devote any appreciable time to parts (C) and (D).

II. DESCRIPTION OF EQUIPMENT

A. The Gas Handling System

The requirements of the gas handling system needed for this project were as follows:

1. Ability to hold a vacuum in the order of 10^{-3} Torr without leaks.

2. Freedom from water, hydrocarbon, or other contamination.

3. Ease of mixing and metering moist and dry gases.

4. Ability to control flow rate through hollow cathode assembly.

5. Ability to obtain constant pressures at various flow rates.

6. Facility of accurate pressure measurement.

7. Ability to supply dry, hydrocarbon-free air.

8. Ability to supply air with a known water concentration.

The schematic diagram of the gas handling system is shown in Figure 1. This unit contained no rubber connections, stopcock grease, mercury, manometer oil, or plastics other than small areas of Teflon bushings and gaskets. The readability of total pressures was to 0.003 Torr full scale.

The system was designed to operate at partial pressures of water vapor down to very low concentrations, i.e., in the parts per million range. The following list of parts refer to this figure.

- A Matheson "Zero Gas" compressed air
- B Catalyst-filled Vycor tube filled with copper turnings
- C Tube furnace
- D Glass bead-filled trap (Dry ice-Acetone) - later replaced as described below.

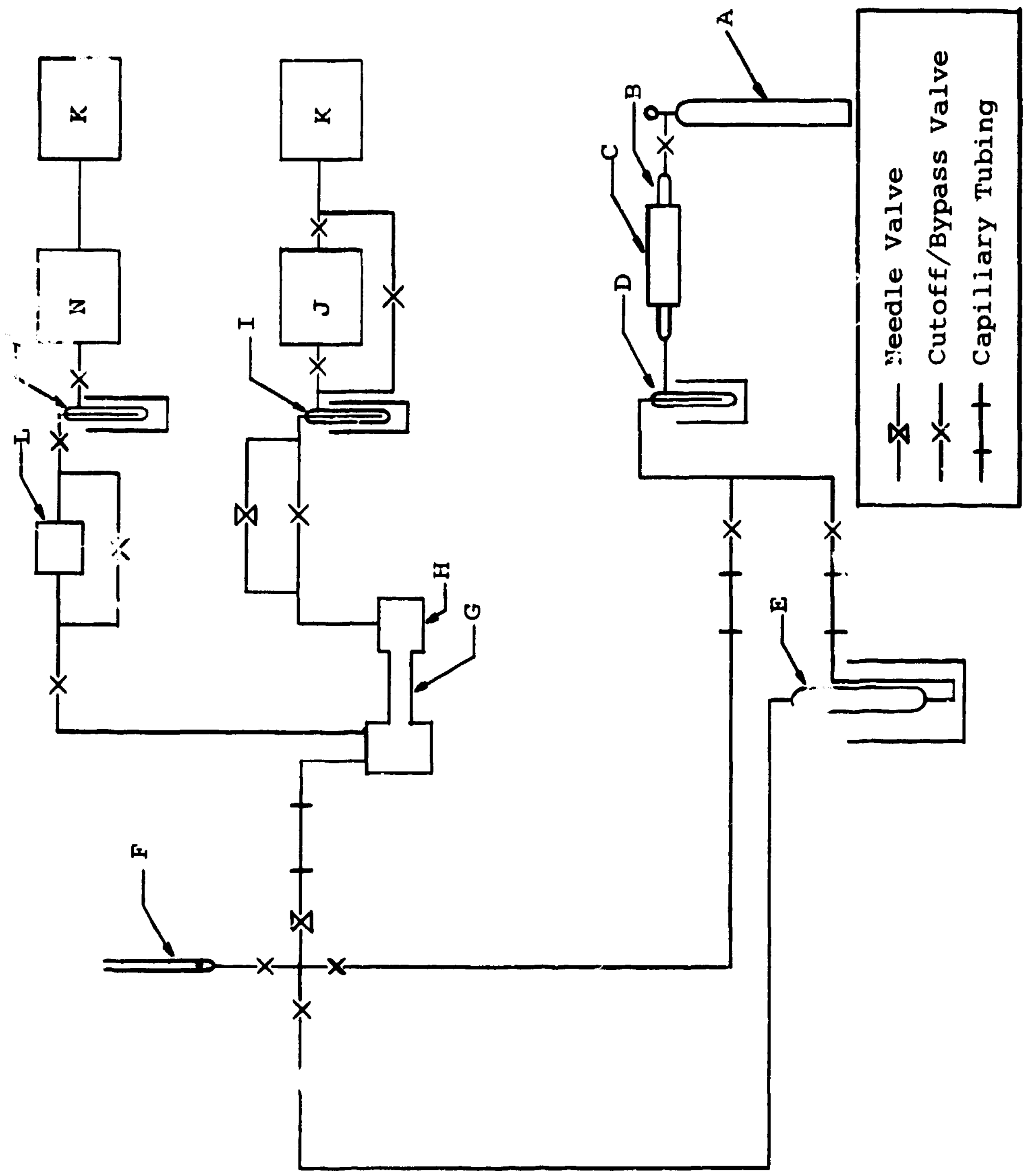


Figure 1. GAS HANDLING SYSTEM

E Ice-filled saturator (Cold Bath)
F Flow meter (0-40 ml/min Air)
G Cathode compartment
H Anode compartment
I Vacuum cold trap (Dry ice-Acetone)
J Oil diffusion pump
K Mechanical vacuum pump
L Baratron Pressure Sensing Head (MKS Baratron Pressure Meter, Type 90M-XRP)
M Vacuum cold trap (liquid nitrogen)
N Mercury diffusion pump.

In operation, Matheson "Zero Gas" compressed air was passed over red-hot copper turnings to oxidize hydrocarbons which were present. The air thus treated was passed through a cold trap packed with 5-mm glass beads at dry ice-acetone temperature. The dried air was then passed through a saturator, filled with finely crushed ice, in a constant temperature bath. By changing the cold bath temperature, different concentrations of water vapor were obtained. Figure 2 shows the theoretical relationship between water vapor concentration by volume and temperature at one atmosphere. The data for this curve were obtained from a chart published by Consolidated Electrodynamics for calculating water vapor concentrations from the dewpoint. To convert parts per million by volume to parts per million by weight, the following formula is used:

$$\text{ppm by weight} = \frac{\text{ppm by volume} \times 18}{\text{mol. wt. of dry air}}$$

The glass bead freeze-out trap, D, was subsequently shown to be relatively ineffective at removing moisture from the air supply. Ice particulate as a result of quick freezing would pass through the glass bead. This trap was replaced with a coil of 1/4 inch o.d. copper tubing packed with activated charcoal and silica gel. The cooling of the coil was accomplished by immersing it in a solid ether cold bath (-105°C). This trap was much more effective.

Pressure measurement was accomplished by the use of an MKS Baratron Pressure Meter, type 90M-XRP with a type 90H-10 pressure head. The Baratron measurements in the vacuum range are independent of the nature or composition of the gas. True pressure (force per unit area) is measured rather than the ionization or thermal equivalents of pressure. Condensable vapors are also measured accurately. Pressure is read on the above instrument directly on a 4-1/2 inch, mirrored, center zero scale meter or as a null bridge. Using the instrument's null bridge function, the manufacturer's calibration data indicate that expected error is in the order of ±0.1%. The principle of operation is to measure the displacement of a

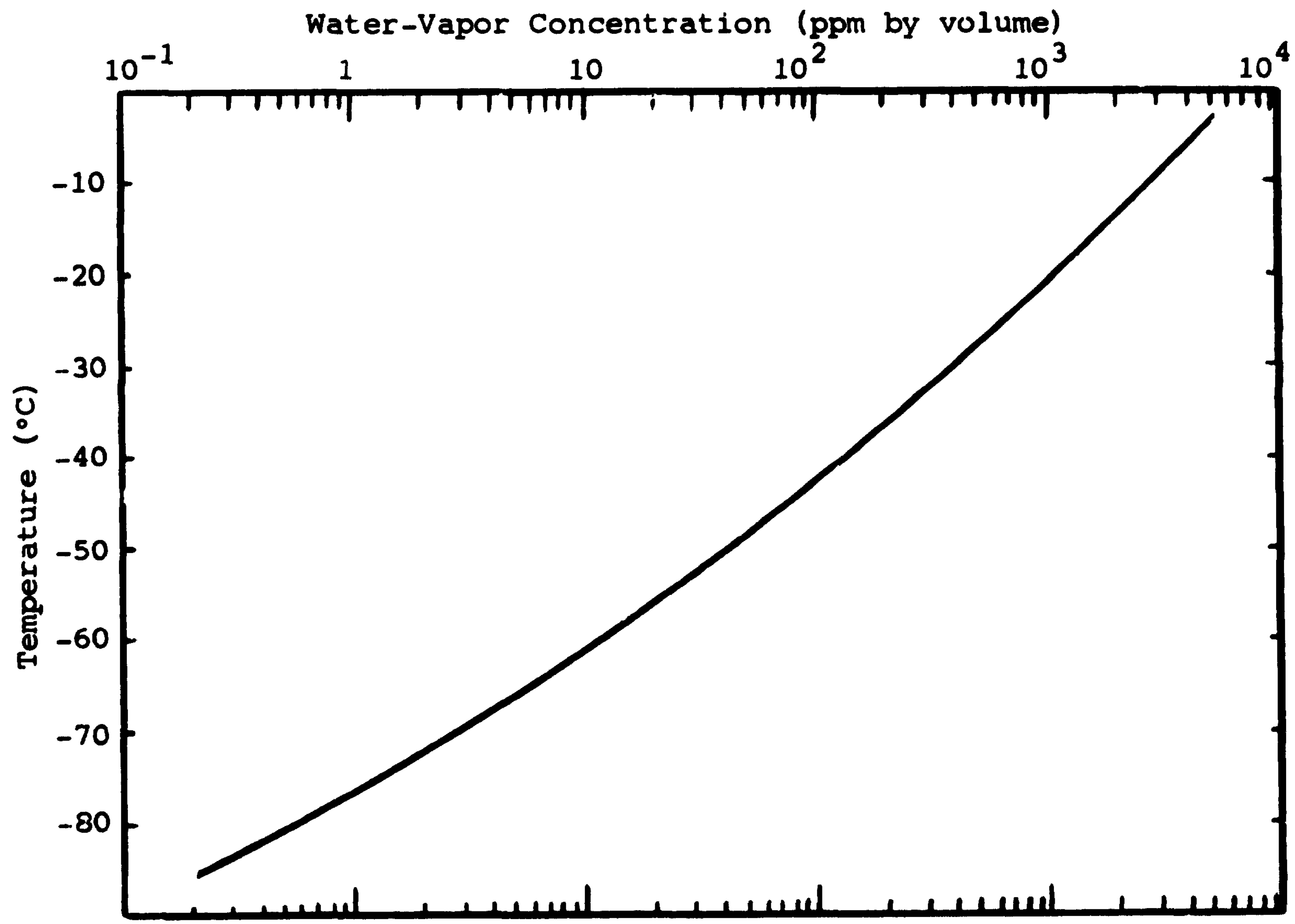


Figure 2. THEORETICAL WATER-VAPOR CONCENTRATION OF SATURATED AIR OVER ICE vs. TEMPERATURE

diaphragm by measuring changes in the capacitance of the system.

B. Electronic System

Two basic detector systems were used in carrying out the experimentation. Both systems used an RCA 7265 photomultiplier as the light sensor. The 7265 is a 14-stage head-on glass tube with S-20 spectral response. The current amplification produced by this tube at the voltages at which it was operated was in the order of 10^6.

Initially a chopped system with a chopping rate of 10 Hz was designed. An amplifier with a bandwidth of 1 Hz with maximum response tuned to 10 Hz was used to drive a chart recorder. This system provided a higher signal to noise ratio than was required. Its disadvantage was the relatively long time constant which gave no indication of instantaneous changes in the discharge intensity.

The system used for most of the work consisted of a dc amplifier used in conjunction with a chart recorder with fast response characteristics. The ac component of the photomultiplier was small enough to permit the manual adjustment of the amplifier zero point to eliminate the dc dark current and still obtain reasonable signal-to-noise ratios.

C. Optical Calibration

The purpose of this phase of work was to calibrate the RCA 7265 photomultiplier tube in order to express the absolute light output due to known water vapor concentrations. A diagram of the device designed for these measurements is shown in Figure 3.

The light source used for the calibration was a 300-watt reflector floodlamp with a frosted face. Light from the lamp was chopped, passed through a Corning #4600 infrared absorbing filter and diffused by a ground glass screen masked by a 1-inch square stop. The purpose of this stop is to cast an image ca. 0.6-inch square on the face of the photomultiplier. The light, after passing through a 6563 Å interference filter with ca. 8-Å bandpass, illuminated the plane of the exit stop. The power density at this plane was determined by mounting an EG&G-SGD-100-Å silicon photodiode, calibrated by the manufacturer in amperes/watt, with known active area, in the exit stop plane. The response curve is shown in Figure 4.

For the calibration, the lamp was placed 670 mm from the ground-glass disk. The power density of the light at the exit stop plane was determined as described above. The photomultiplier

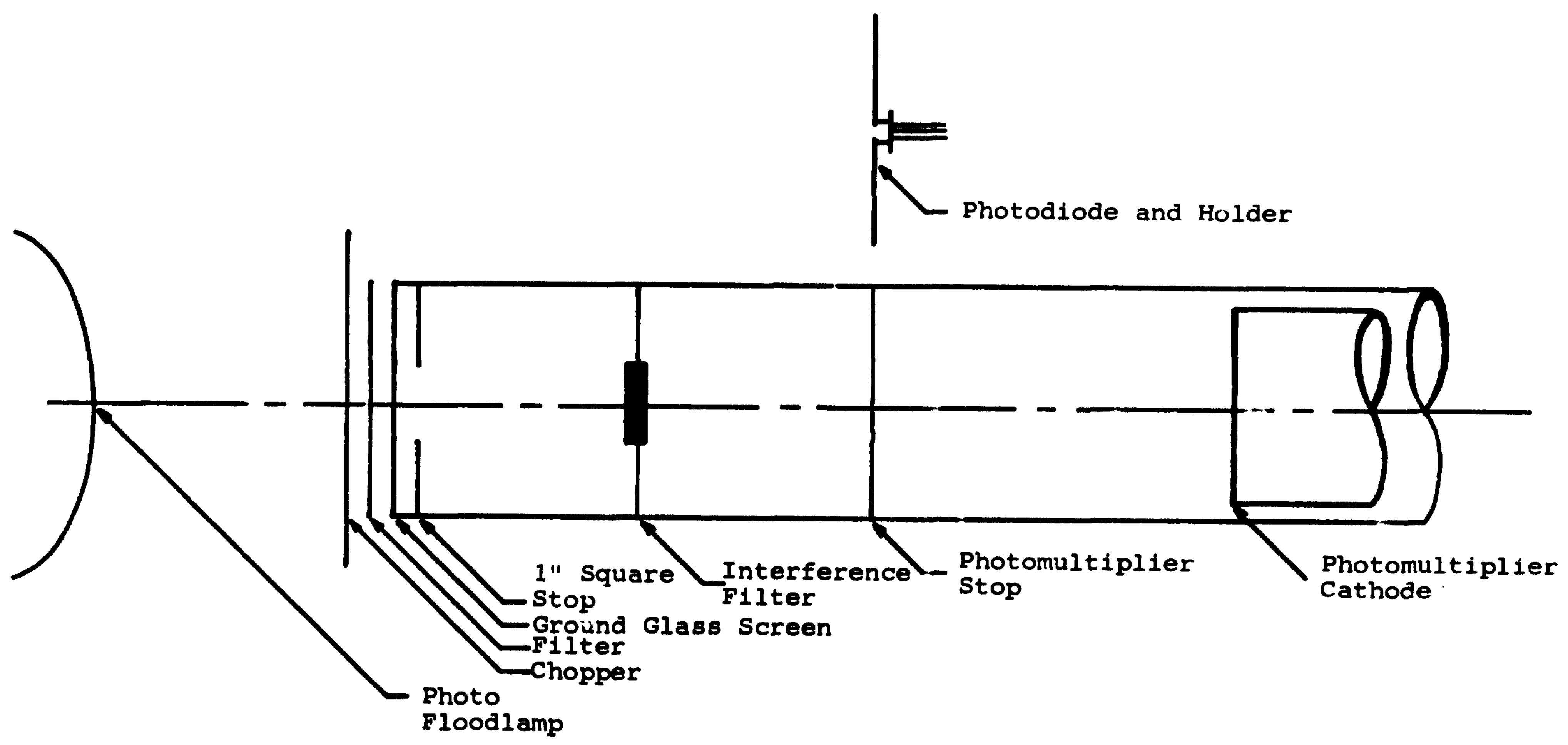
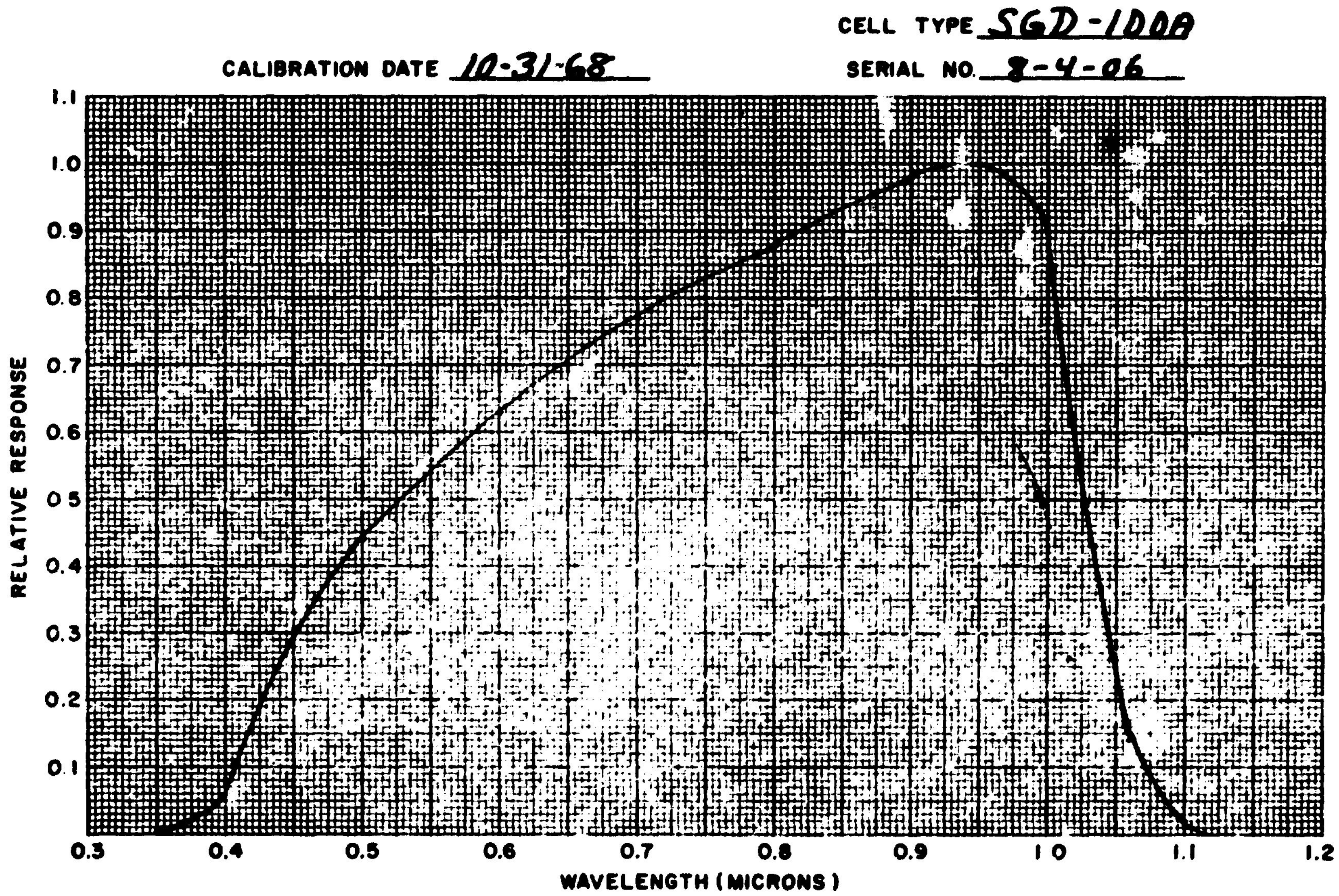


Figure 3. APPARATUS FOR ABSOLUTE INTENSITY CALIBRATION



ABSOLUTE RESPONSIVITY = .530 μA/μWATT @ 0.95 MICRONS

ACTIVE AREA = 0.0507 CM²

Figure 4. RELATIVE SPECTRAL RESPONSE CURVE

fitted with a 2 x 0.06 mm stop then replaced the photodiode. Peak-to-peak readings of the output of both the photodiode and photomultiplier were made using an oscilloscope and the results calculated to express photomultiplier output in terms of amperes per watt.

Figure 5 shows the absolute responsivity of the 7265 RCA photomultiplier versus applied voltage. The responsisivity is equal to the maximum nominal value quoted by the manufacturer. The departure from linearity at high PM bias is systematic. At these intensities the signal is large enough to appreciably alter the bias on the anode and on the last dynode.

III. EXPERIMENTAL RESULTS

A. Cathode Geometry

The initial studies on cathode design were carried out using the unit shown in Figure 6. This was a modification of the unit used by McNalley et al. (1) for lithium isotope assay and was a design used to monitor the major constituents in cabin atmospheres (2) at intermediate pressures, i.e., 0.2 to 0.3 Torr. An advantage of this design was that the cathode could be quickly and easily changed. Any geometry which could be machined into a 1/2-inch diameter rod shorter than 1-1/2 inch could be studied.

The first geometry used was a gold foil lined cylindrical cathode ca. 5-mm diameter by 14 mm deep. The anode chamber was also gold lined. The total pressure was varied from 0.1 to 10 Torr using ambient air at ca. 7% absolute humidity. An EMF of 2000 volts was established between the anode and cathode. The power supply was set to deliver 10 ma. At intermediate pressures the cathode cavity appeared to be uniformly illuminated with a reddish-purple glow. At low and high pressures in the range, the radiance was nonuniformly distributed. The lower pressure discharges appeared as a central bright spot with another less intense glow extending from the spot to the walls of the cathode. Increasing pressure caused this spot to become less intense and tend toward the uniformity of radiance mentioned above. At pressures of ca. 3 Torr and above, a central dark spot formed.

A spectrographic plate showed the hydrogen line at 6562.8 Å at all pressures and a background spectrum attributed to nitrogen at pressures greater than 0.5 Torr. At 0.1 and 0.2 Torr the hydrogen line was conspicuous and the nitrogen structure appeared to be absent despite an increase of exposure time from 30 to 60 seconds. The hydrogen line was much less intense at 0.1 than at 0.2 Torr.

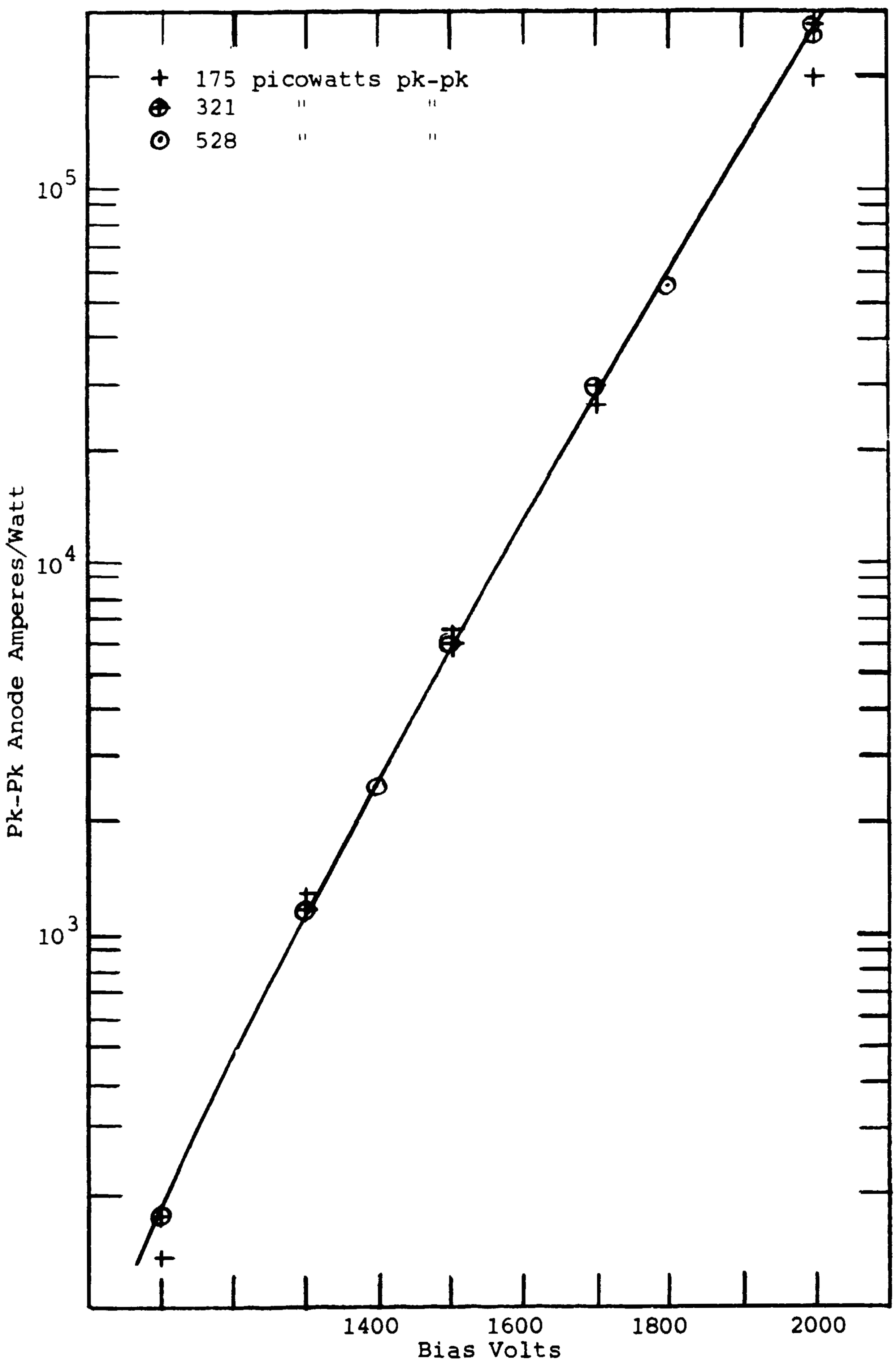


Figure 5. ABSOLUTE RESPONSIVITY OF RCA 7265 PM TUBE

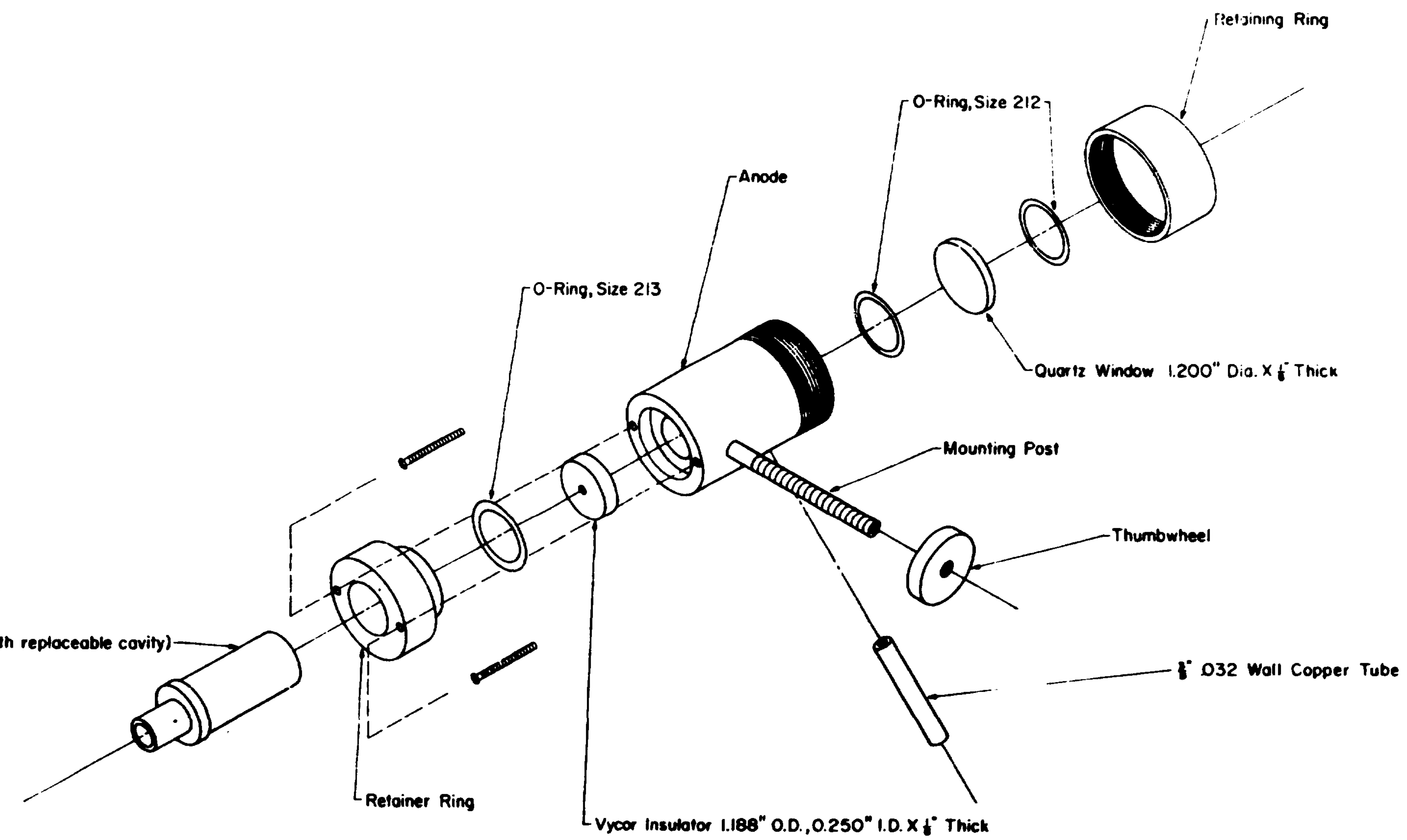


Figure 6. EXPLODED VIEW OF LIGHT SOURCE

Since optimum cathode diameter approximates electron mean free path, variations in behavior were expected over the 100-fold pressure range of interest. The cathode glow originates within the hollow portion of the cathode. Previous work (2) indicated maximum intensity for a given concentration when depth approximates twice the diameter

From the above observations, it was expected that a conical cavity would provide a range of proportionate depths and diameters. A cavity with a 60° cone with an entrance diameter of 1 cm was machined from an aluminum cylinder. With this geometry the bright spot persists to higher pressures than previously. The dark spot could not be produced consistently at the continued higher pressures.

Since the conical geometry seemed to produce a more uniform discharge over the pressure range, additional experimentation was continued with 0° (cylindrical), 30° and 60° cone geometries. The electrical characteristics for the cylindrical and 30° cones showed a quite well defined constant-voltage plateau for the pressures of 0.5, 1.0 and 8 Torr. Figure 7 shows the increasing positive slope as the pressure is reduced for the 60° cone cathode.

A spectrographic examination of the light emitted at 6562.8 Å with respect to pressure showed the output of the 30° cone to be more uniform than that of the cylindrical (0°) or 60° conical cathode.

The initial experiments were conducted at an EMF of less than 800 volts. At voltages higher than this, electrical breakover occurred in the system resulting in parallel discharges. These discharges used power that would normally be used by the cathode discharge. At the same time there was a marked decrease in the output of the light intensity.

The air was drawn into the anode and exhausted around the cathode, Figure 6. The primary location of these discharges was the insulating glass tube connecting the cathode to the metal exhaust tube. The application of large EMF across this insulator caused the potential gradient to exceed the threshold required to produce ionization of the gas molecules and thus a discharge results. This situation was eliminated by lengthening this tubulation by a factor of four, which decreased the potential gradient to a point where ignition would not take place.

After this modification, application of greater EMF's showed that some sites of parallel discharge still existed. These were the ports in the cathode holder which permitted gas flow around, rather than through the cathode. The cathode holder was redesigned to eliminate these ports. The system

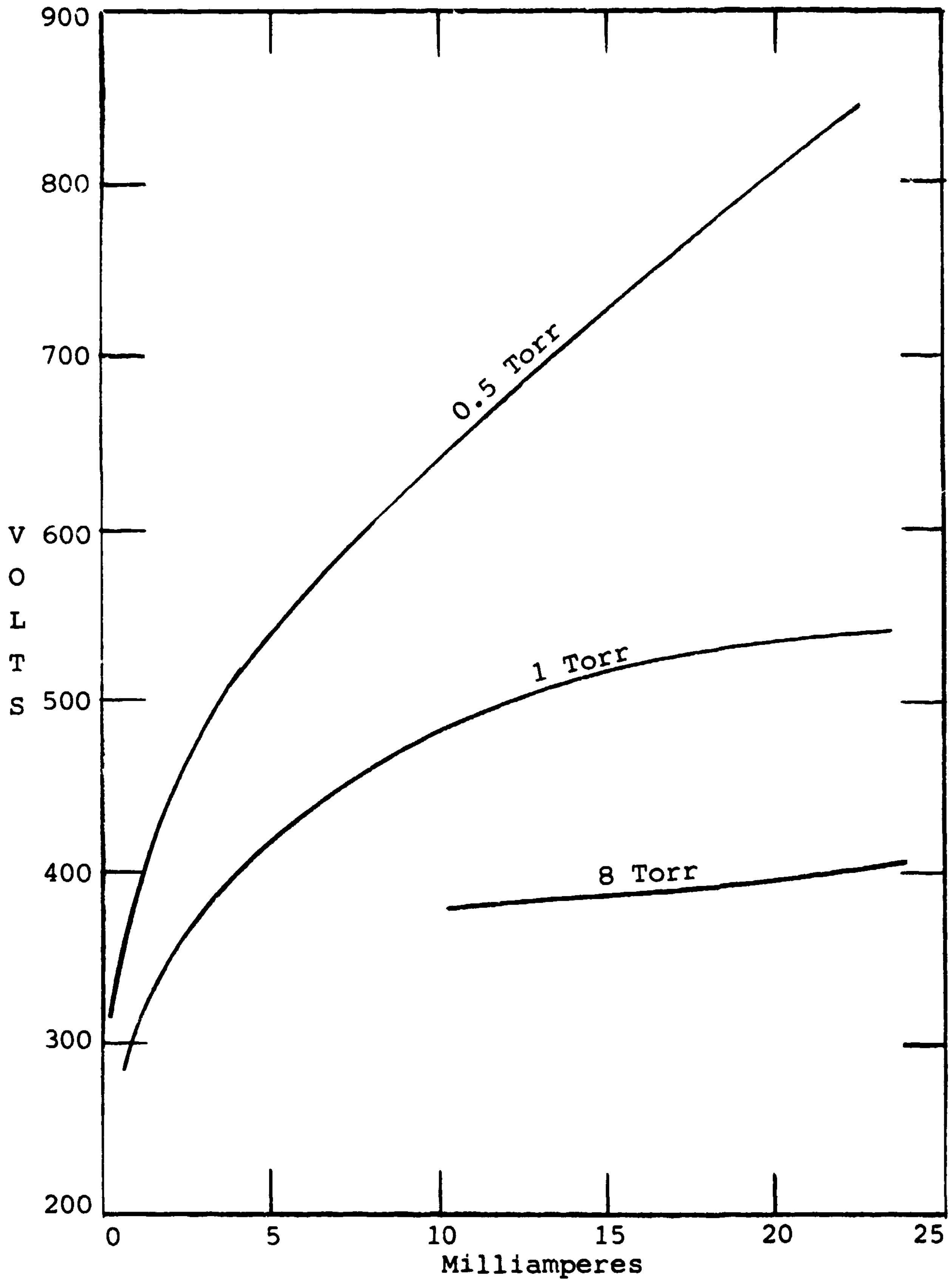


Figure 7. CURRENT-VOLTAGE CURVES, 60° CONE

incorporated a "flow-through" configuration in which the gases passed directly through the cathode.

Prior to the above modifications, the light output for the 6562.8-Å hydrogen line was of usable intensity only between ca. 0.4 and 3 Torr. With these changes, the range was extended to less than 0.1 Torr with 2000 volts applied to the cathode.

Several configurations of the flow-through cathodes were explored. These were of the general type shown in Figure 8, differing only in the angle Q. Room air was used at this time which had an absolute humidity of approximately 1%.

In most of the cathodes studied, there were pressures at which the electrical characteristics and the hydrogen line intensity would change abruptly. This change was caused by the discharges entering the #50 through-drilled hole while scanning the pressure range from the low to the high end. The point at which the change takes place is influenced by current density in the discharge as well as the angle of the cone.

The data indicate for the geometries studied that the higher the current density, the lower the pressure required to cause this transition to take place. Other experiments have shown that varying hole size also changes the pressure at which this transition takes place. With this transition taking place it would be difficult to maintain calibration of the device, and thus this type of flow-through configuration is not well suited for this application.

The next geometry studied was the one in which the cathodes were open at both ends and enclosed in a glass envelope. The first experimental cathode was copper, 1/2-inch diameter and 1 inch in length. Upon application of 2000 volts EMF at low pressure, the discharge lit up most of the glass envelope in which the cathode was contained with a pale bluish glow. As the pressure was increased, this glow became more intense. Increasing the pressure further caused the glow to move closer to the cathode until (at approximately 1 Torr) the discharge was only in and around the cathode. Further increase in pressure caused the glow inside the cathode to become more faint (as well as toroid shaped) until at ca. 5 Torr the inside of the cathode appeared to the eye to be completely dark while the outside was still glowing brightly. Increasing the pressure beyond this point caused parts of the exterior of the cathode to stop glowing until at ca. 12 Torr most of the outer surface of the cathode was dark. It was found that by increasing the current density in the discharge, the glow could be kept inside the cathode until higher pressures were reached. This cathode was rather short lived. The current densities required to keep both the inside and the outside of the cathode glowing were sufficient to heat the cathode to the melting point of the

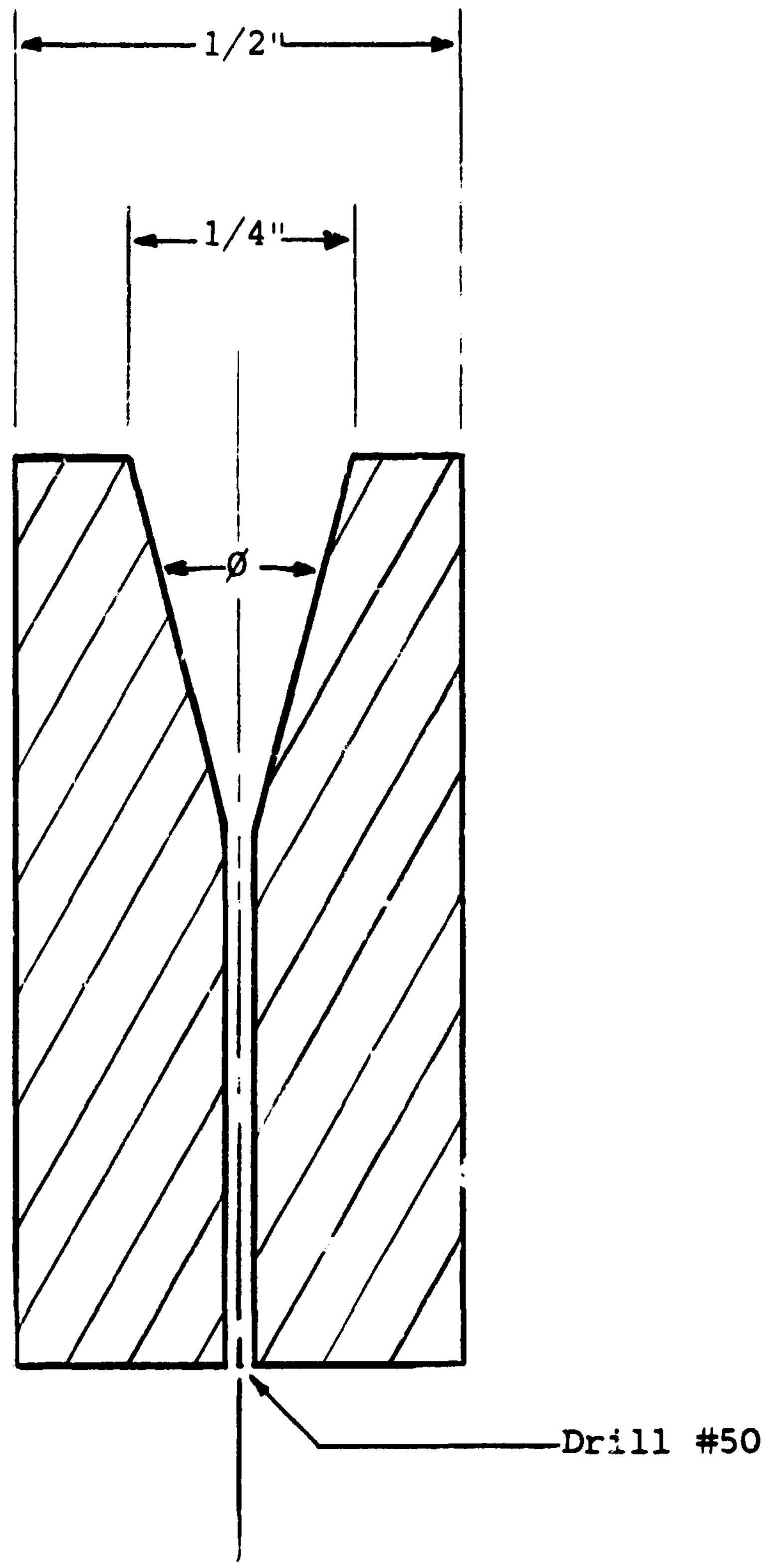


Figure 8. TYPICAL FLOW THROUGH CATHODE DESIGN
(Ø = 30°)

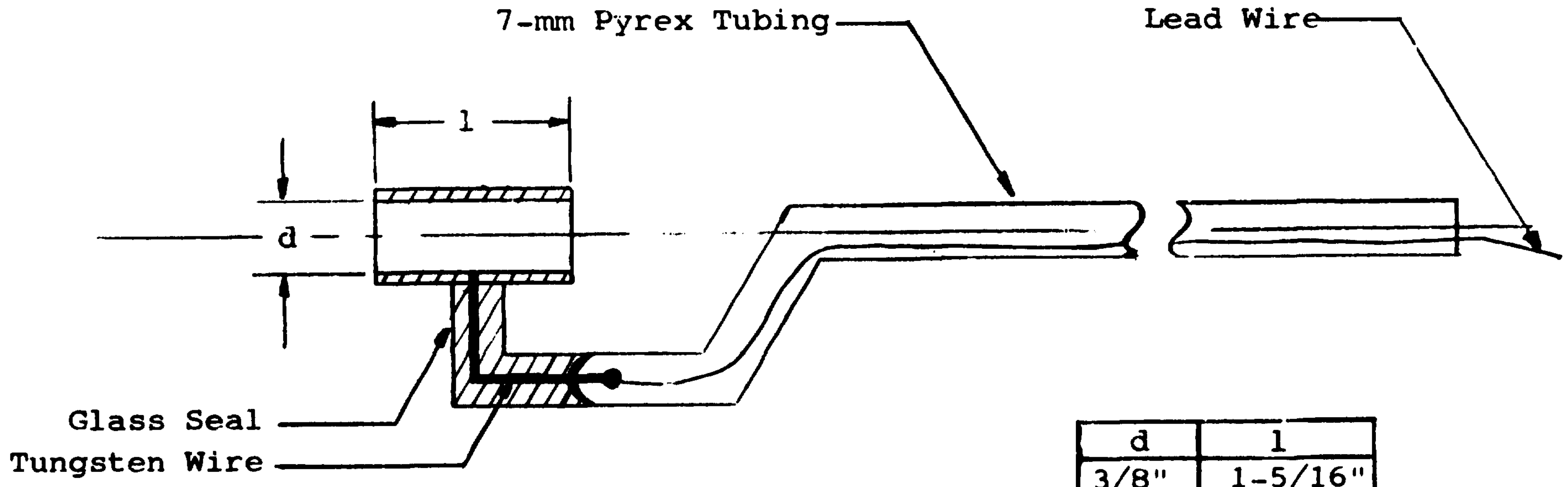
silver solder used to hold the cathode to its electrical contact and support wire. The light output, when the discharge was on, appeared to be at least as bright to the eye as in the other cathode configurations tried to date, so experimentation was continued.

A series of three different tantalum-lined glass cathodes were designed, Figure 9, and mounted, Figure 10, so that the electrical parts could be easily changed. All metal parts of the cathode except the end of the tungsten wire and the tantalum foil liner are insulated from the vacuum chamber. The vacuum seal is made near the open end of the 7-mm Pyrex tube. The anode was a #14 copper wire ring, 2-1/4 inches in diameter, that could be held in different positions with respect to the cathode.

The photographs for the following discussion were taken with a Polaroid Model 110B camera using No. 47 high-speed film. Time and stops were 1/15 sec and f/32. All end-on views were taken with the Polaroid plus four closeup lens, nine inches away from the cathode and through a Corning 2-73 filter. This was done in an attempt to match the film record more closely to what the eye observed.

For each cathode configuration at the lower pressures, the discharge extended well in front and behind the cathode regardless of the anode position. This is illustrated in Figures 11, 12, and 14. At the higher pressures its position appeared to determine whether the discharge appeared at the front or rear of the cathode, Figures 16 and 17.

An observation which is not particularly clear in the photographs is the presence of a thin relatively intense line which extends down the center from the front to the back of the cathode at the lower pressures. At slightly higher pressures, the thin line is replaced by an apparently solid discharge column, which also appears in the center without touching the walls of the cathode. By this time the discharge has almost completely moved into the cathode, Figure 15. At still higher pressures, the center of this column seems to fade and the discharge expands outward toward the walls of the cathode, thus forming a toroid-shaped discharge, Figures 16 and 17. At the same time the discharge appears to shrink in length. In the case of the 3/8-inch diameter cathode, this expansion and shrinking continues until at ca. 8 to 12 Torr, part of the discharge is extinguished and a crescent-shaped glow persists apparently in contact with the wall of the cathode, Figure 17. It should be noted that in the 1/4-inch diameter cathode, Figure 13, at 10 Torr the discharge is still in the form of a relatively bright toroid. Also note that at 0.5 Torr, the 1/4-inch diameter cathode still exhibits the same characteristics that it did at 0.2 Torr except for increased intensity,



d	l
3/8"	1-5/16"
3/8"	7/16"
1/4"	1-1/16"

Figure 9. TANTALUM-LINED GLASS CATHODE CONSTRUCTION

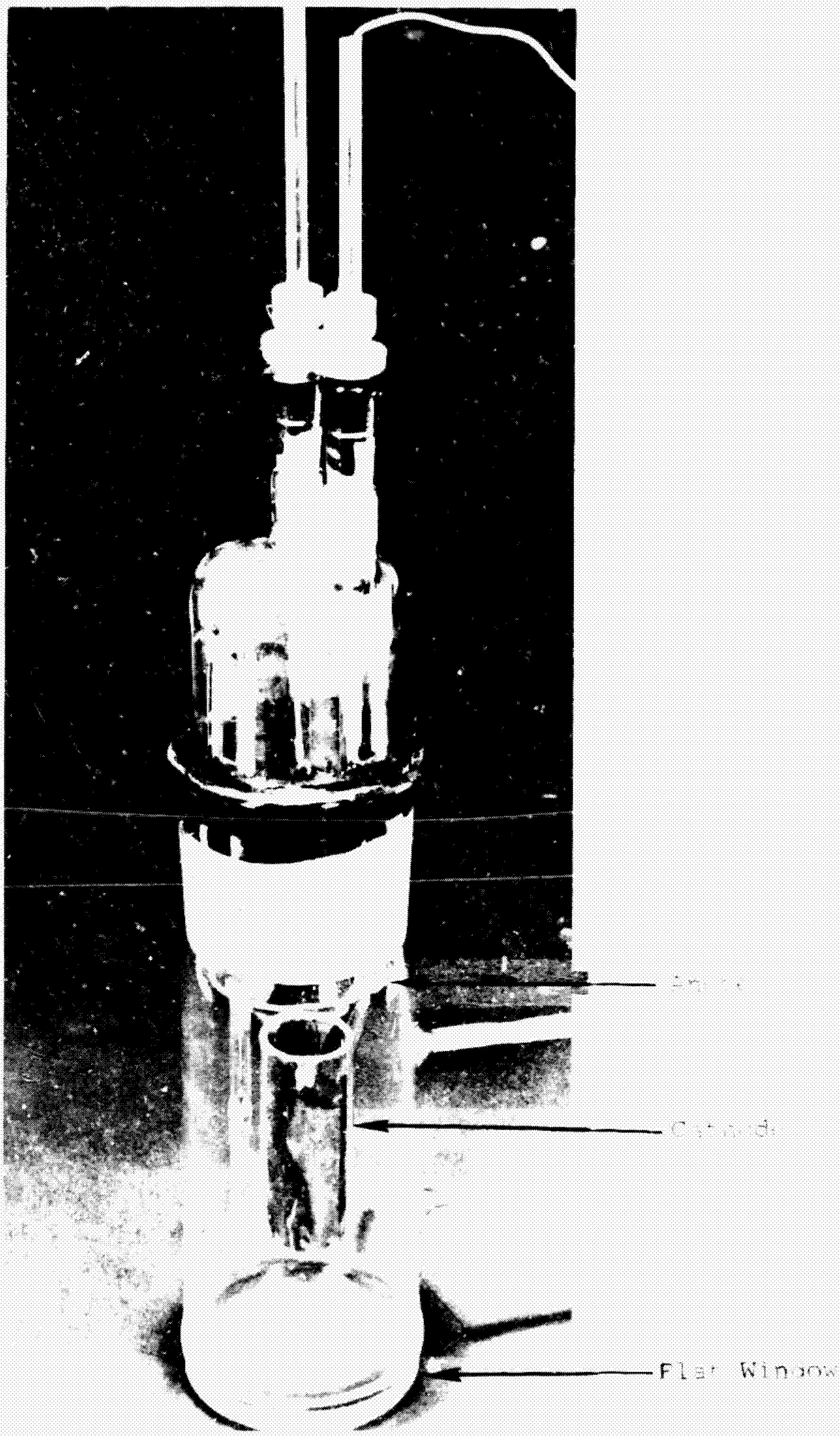
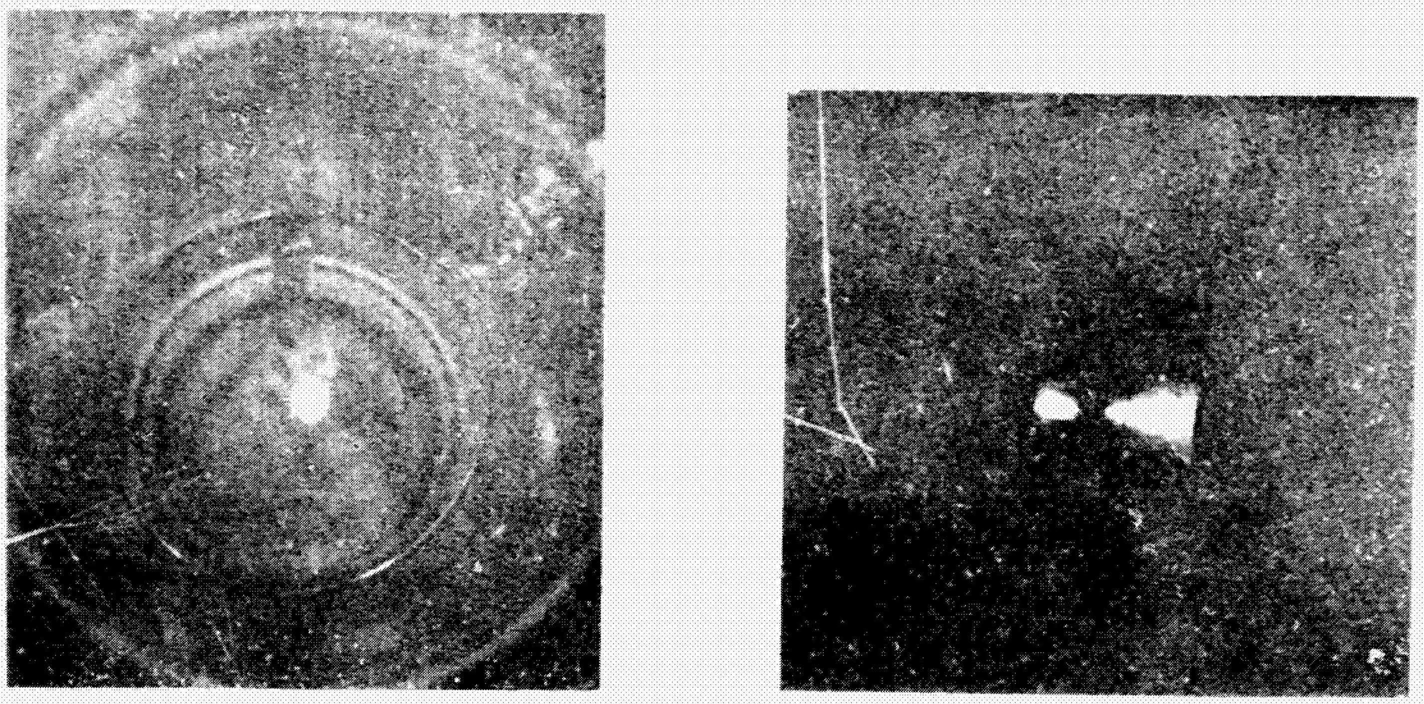


Figure 10. HOLLOW-CATHODE CELL

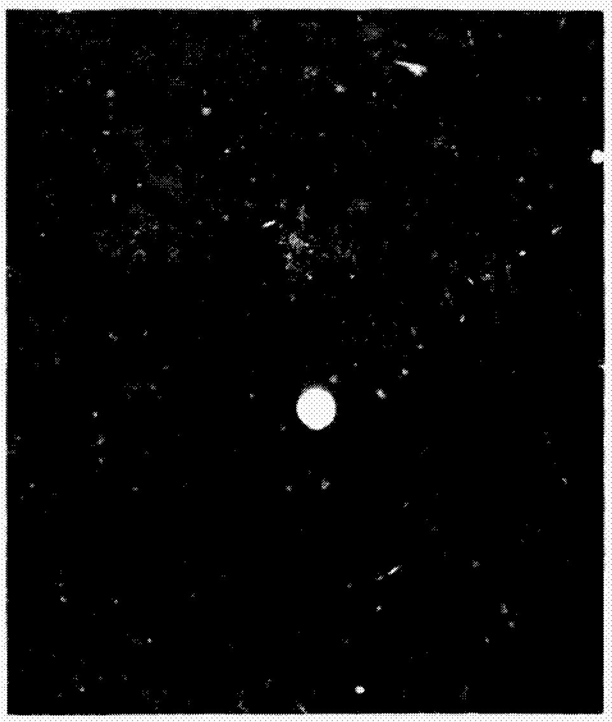
Anode in Front of Cathode

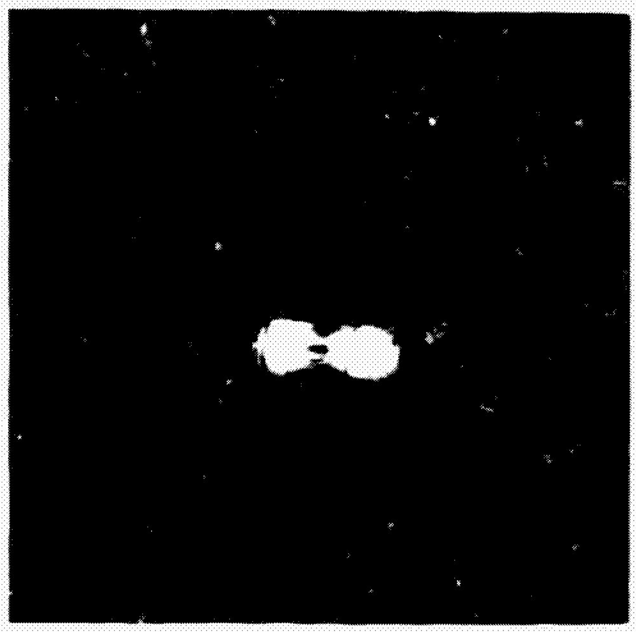


A 0.2 Torr B

Figure 11. POSITION OF ANODE, 0.2 TORR,
1/4" DIAMETER CATHODE

Anode in Front of Cathode





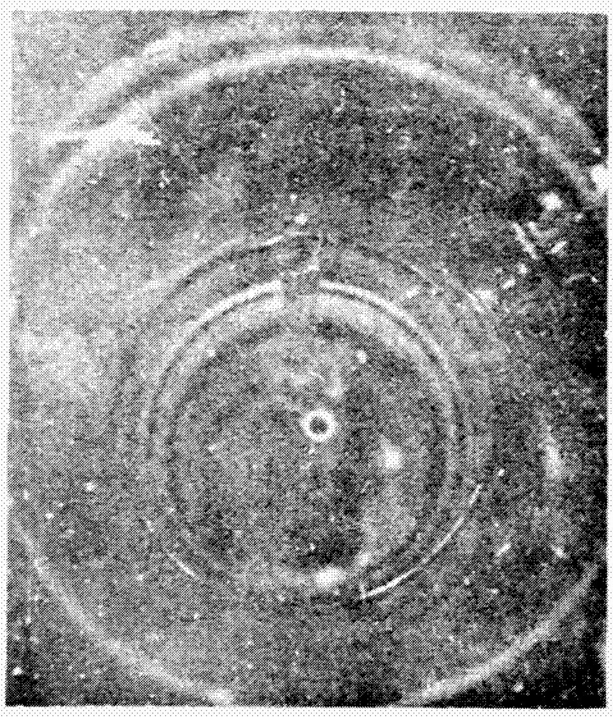
A 0.5 Torr B

Figure 12. POSITION OF ANODE, 0.5 TORR, 1/4" DIAMETER CATHODE

Anode in Front of Cathode

A. 2.0 Torr

B. 5.0 Torr

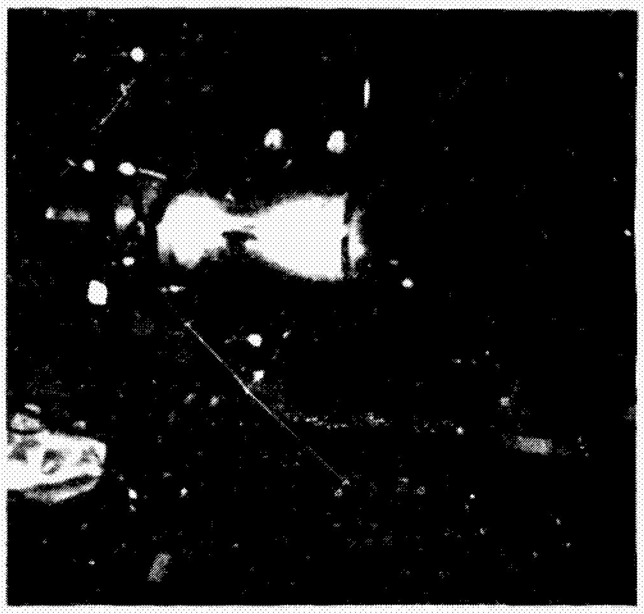


C. 10.0 Torr

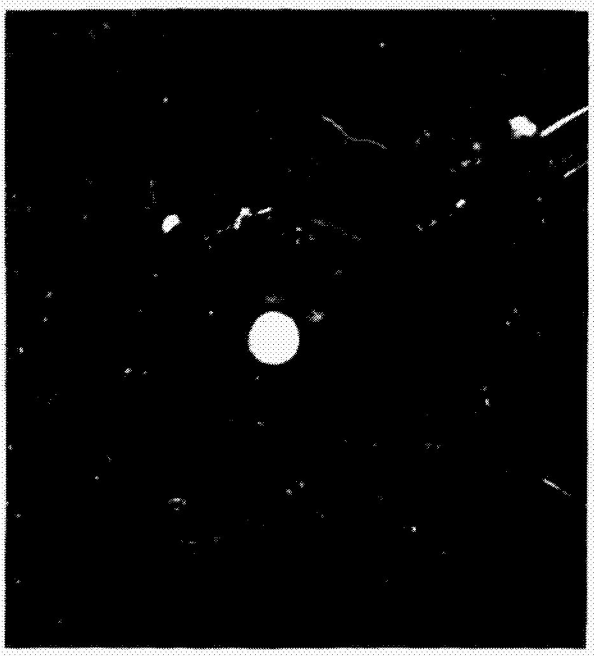
Figure 13. INFLUENCE OF HIGHER PRESSURES,
1/4" DIAMETER CATHODE

Cathode Centered in Anode

Anode in Front of Cathode



A



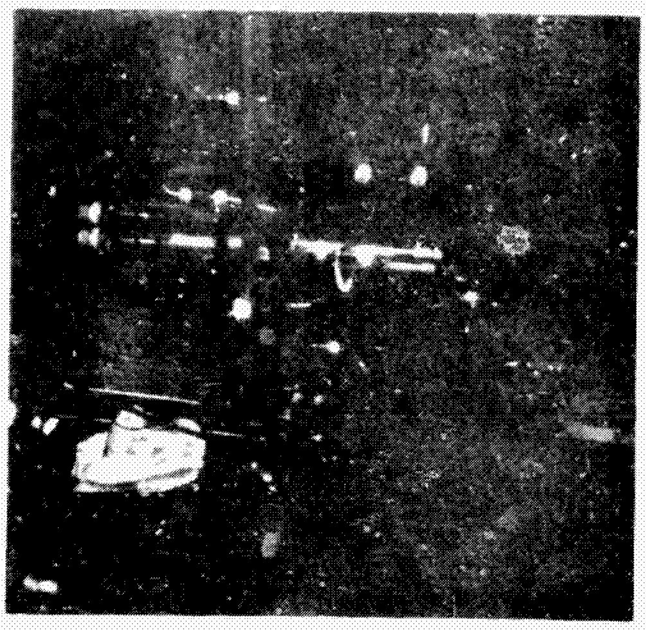
B

C

Figure 14. INFLUENCE OF ANODE, 0.2 TORR,
3/8" DIAMETER CATHODE

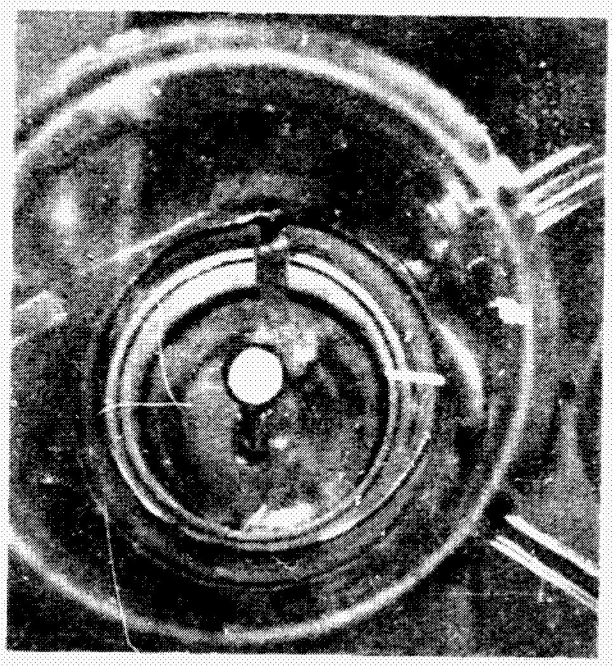
Cathode Centered in Anode

Anode in Front of Cathode



A

B

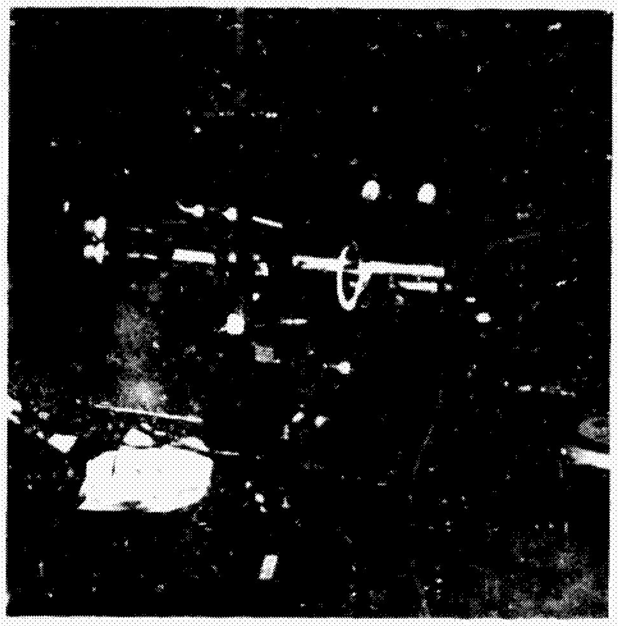


C

Figure 15. INFLUENCE OF ANODE, 0.5 TORR,
3/8" DIAMETER CATHODE

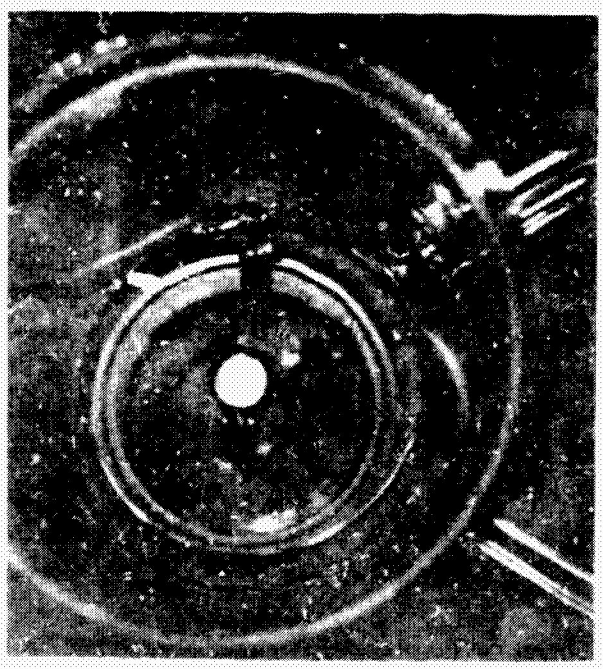
Cathode Centered in Anode

Anode in Front of Cathode



A

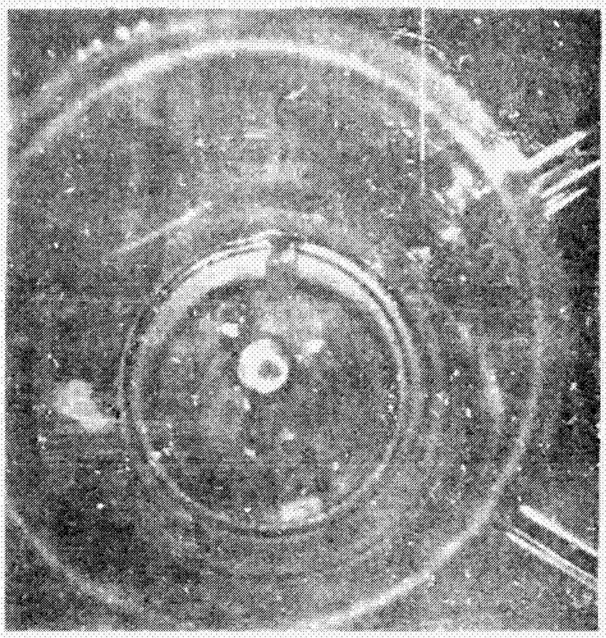
B

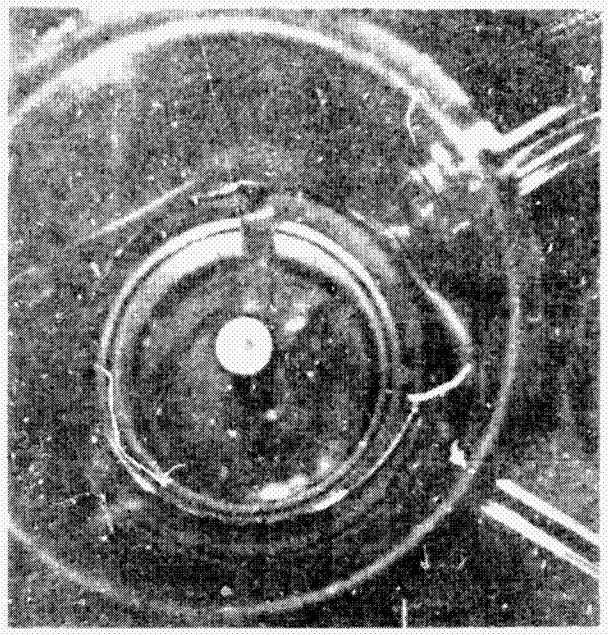


C

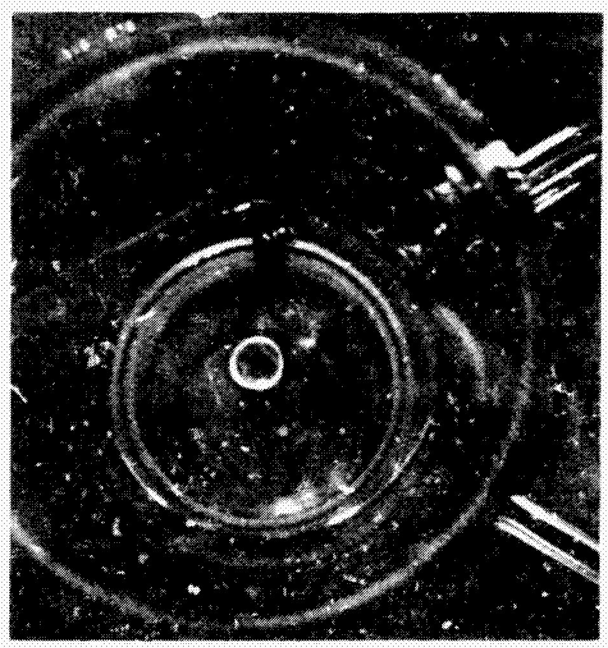
Figure 16. INFLUENCE OF ANODE, 2.0 TORR, 3/8" DIAMETER CATHODE

Cathode Centered in Anode | Anode in Front of Cathode





A | 5.0 Torr | B



C | 10.0 Torr | D

Figure 17. INFLUENCE OF ANODE, 5.0 and 10.0 TORR, 3/8" DIAMETER CATHODE

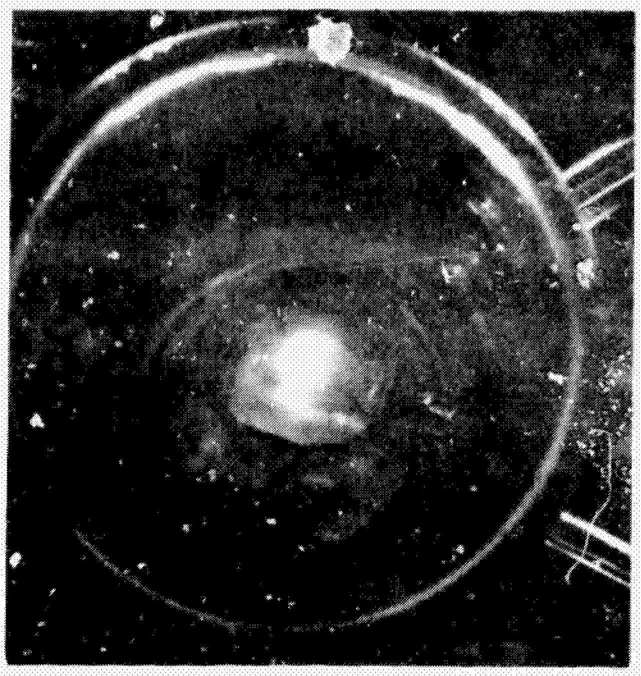
Figures 12 and 13. It has also been observed that a faint discharge is present in the 1/4-inch cathode at pressures below 0.04 Torr.

As previously discussed for the tubular cathodes at pressures lower than ca. 0.5 Torr, the discharge consisted of a very thin line through the center of the cathode. As the pressure was increased to ca. 0.5 Torr, the discharge abruptly changed shape and electrical characteristics. The discharge then appeared to be a solid concentric cylinder within the cathode, with a noticeable annular dark space between the discharge and the interior cathode wall. Decreasing the cathode diameter caused this transition to occur at higher pressures. Therefore larger cathode diameters were examined to extend the range of the cylindrical discharge mode below 0.5 Torr.

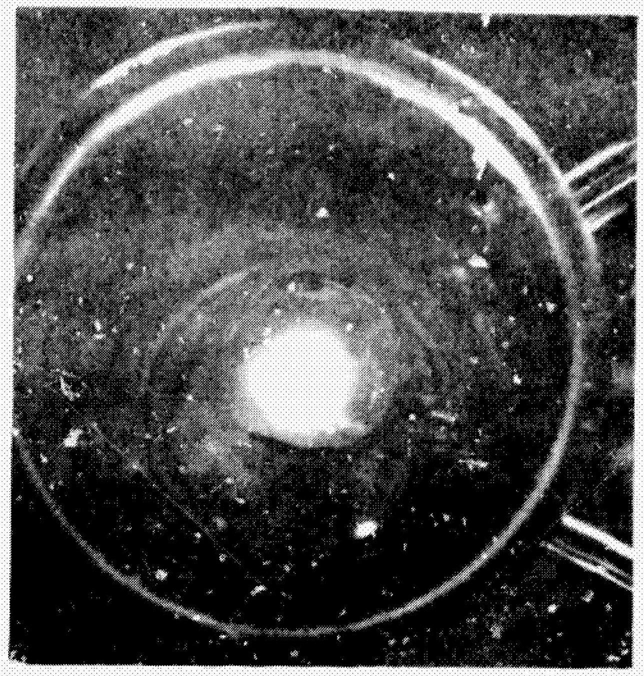
The first large diameter cathode was 1 inch diameter by 1 inch long and was of the type described in Figure 18. The discharge changed from a dim fine line to an intense cylinder at ca. 0.13 Torr. As previously noted, a large portion of the cylindrical discharge also extended in front of and behind the cathode. The next geometry underwent transition at ca. 0.08 Torr with 2000 volts applied EMF. It should be noted that although the discharge while in the cylindrical form requires only ca. 500 volts EMF to operate through most of the range, the 2000 volts is required to obtain sufficient current densities to cause the transition to take place.

As observed with the other right cylindrical geometries, the 1 inch by 2-1/2 inch cathode exhibited several types of discharge. At low pressures the discharge was a faint thin line through the center of the cathode, Figure 18A. As the pressure was increased, the discharge abruptly changed to a solid cylinder that extended the length of the cathode. Increasing the pressure further caused the discharge diameter to increase, Figure 19. At ca. 0.5 Torr the discharge appeared to the eye to be less intense in the center. Increasing pressure above 0.5 Torr caused the center of the discharge to become less intense as well as shrink in length to form a toroid at the anode end of the cathode, Figures 20 and 21. At ca. 2.5 Torr, part of the toroid extinguished to leave a crescent-shaped discharge, Figure 21.

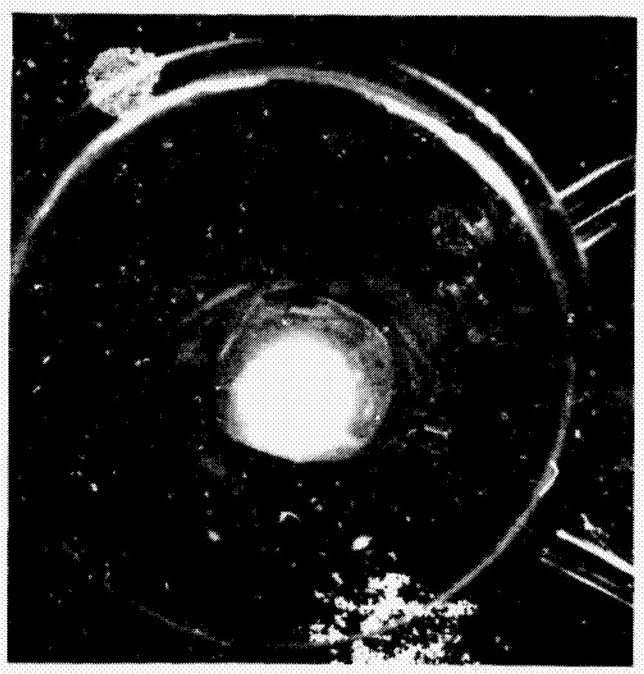
The relative intensity of the 6562.8-Å hydrogen and the 6614-Å nitrogen bandhead are plotted with respect to pressure, Figure 22. The variation in current, voltage and power are also included. It is to be noted that the relative spectral intensity for hydrogen is the greatest at the low pressures and decreases as the pressure increases, while the relative intensity for nitrogen passes through a maximum at about 0.25 Torr. The large change in the voltage-current response at 2.5 Torr corresponds to the formation of the crescent-shaped



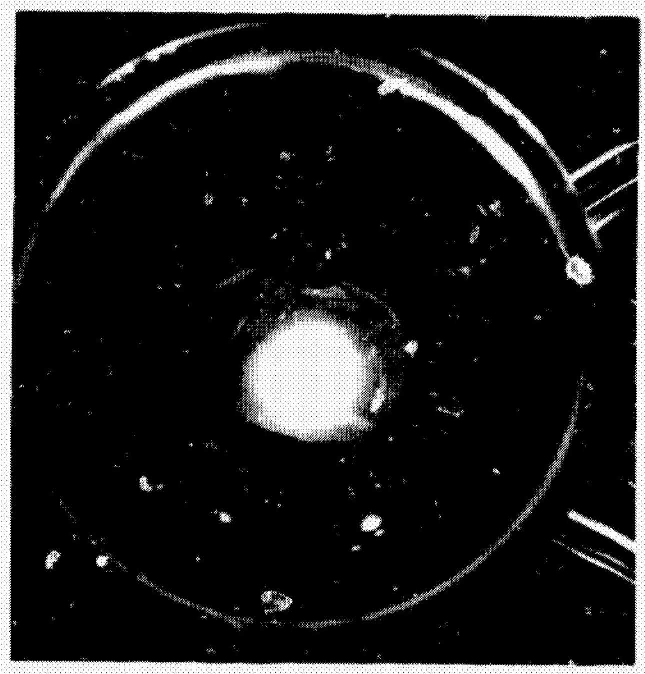
A. 0.08 Torr



B. 0.09 Torr



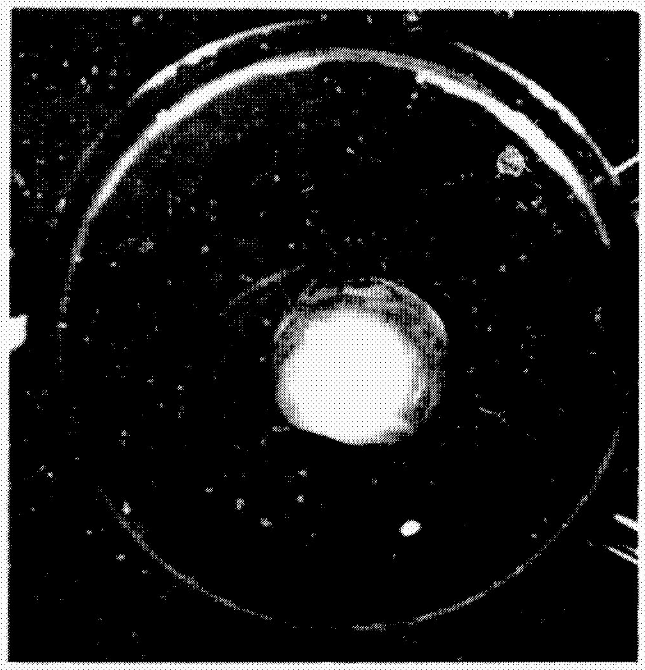
C. 0.1 Torr



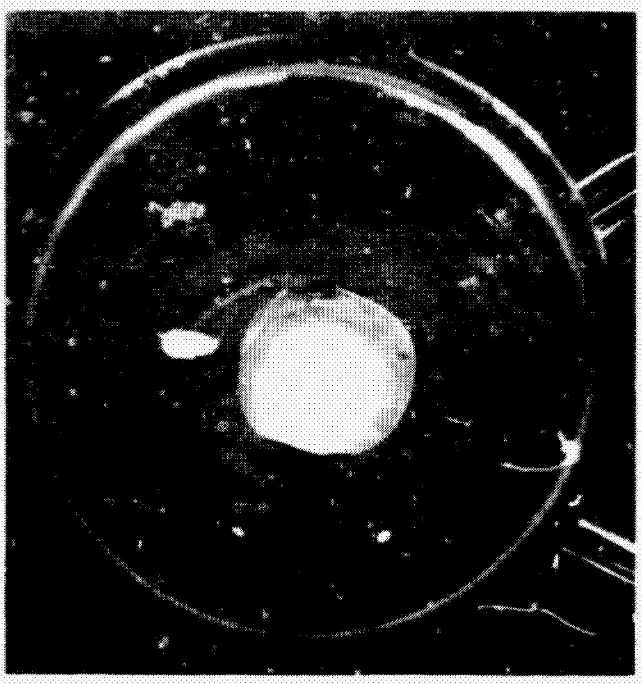
D. 0.15 Torr

Figure 18. INFLUENCE OF PRESSURE, 0.08-0.15 TORR, 1" DIAMETER CATHODE

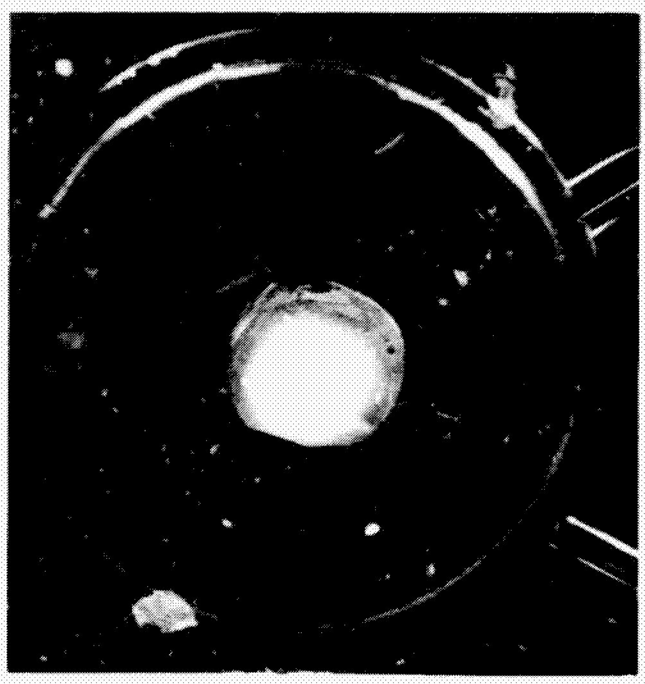
A. 0.2 Torr



B. 0.3 Torr



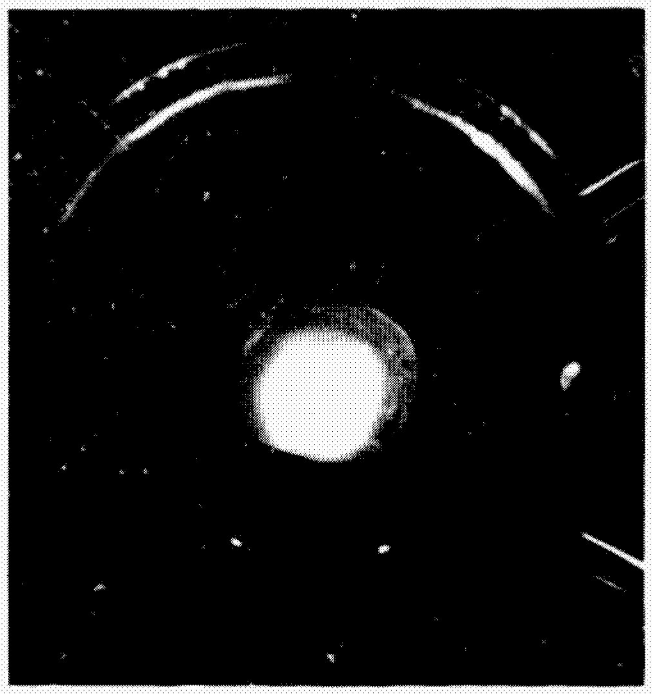
C. 0.4 Torr



D. 0.5 Torr

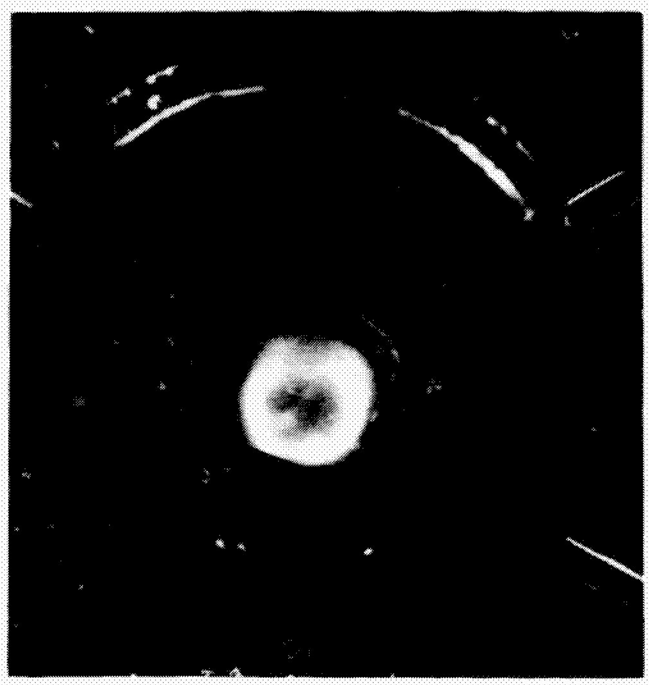
Figure 19. INFLUENCE OF PRESSURE, 0.2-0.5 TORR,
1" DIAMETER CATHODE

A. 0.6 Torr



B. 0.7 Torr

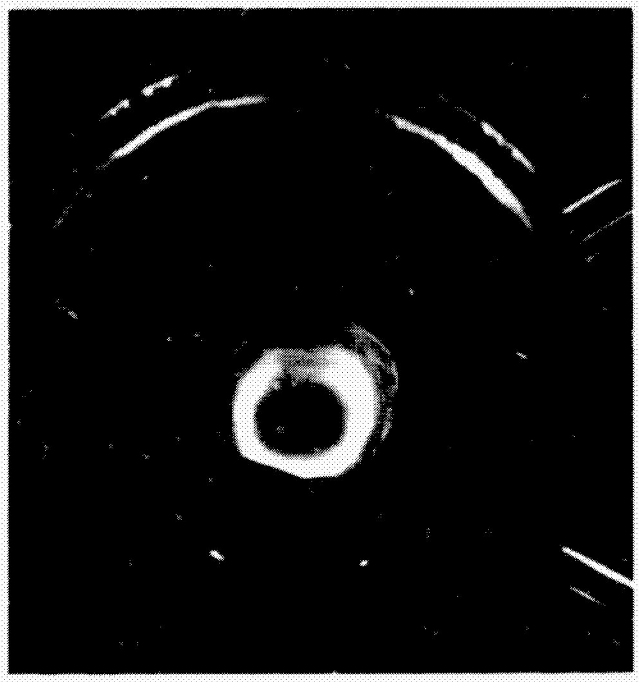
C. 0.8 Torr



D. 0.9 Torr

Figure 20. INFLUENCE OF PRESSURE, 0.6-0.9 TORR, 1" DIAMETER CATHODE

A. 1.0 Torr

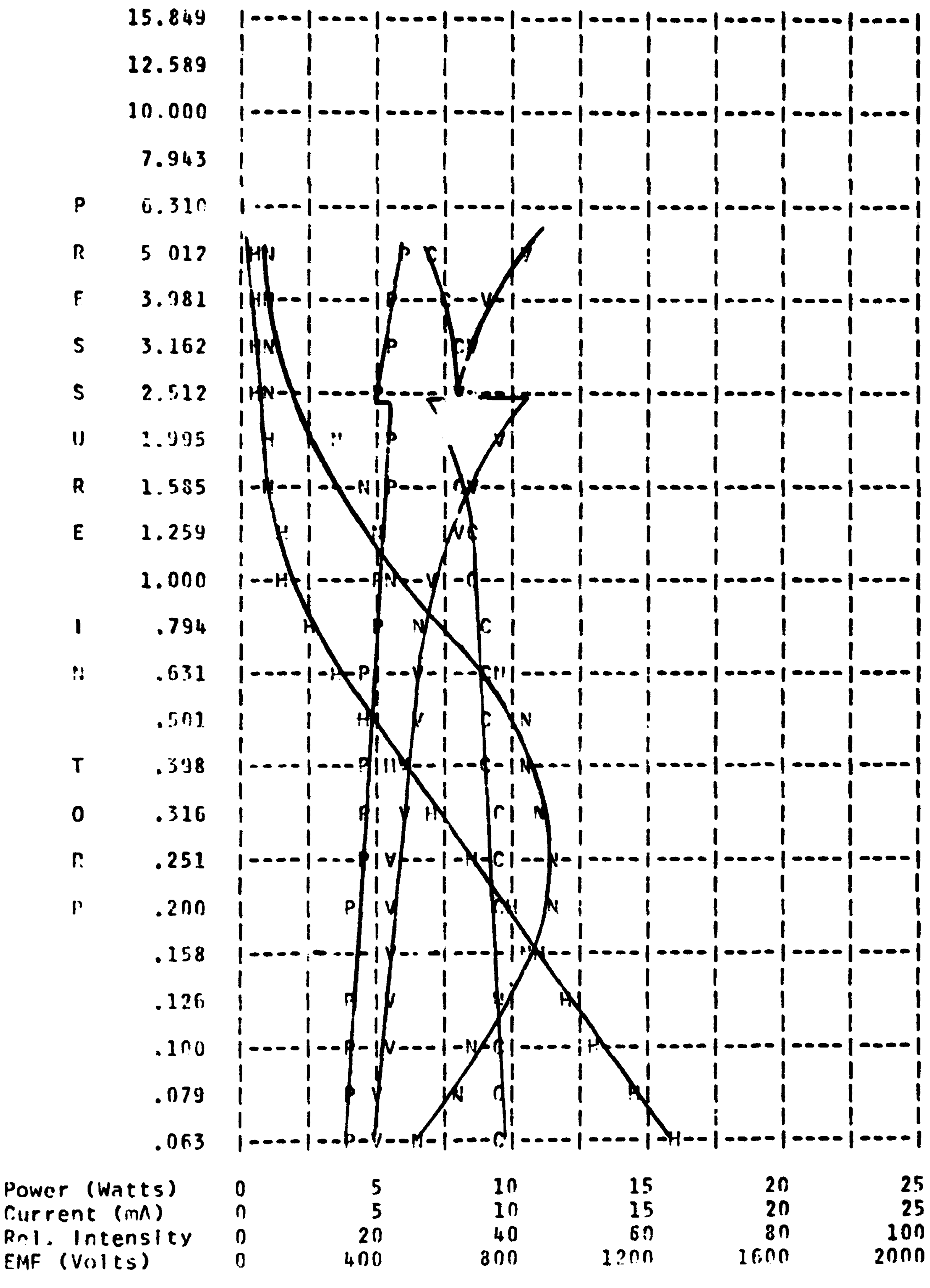


B. 1.5 Torr

C. 2.0 Torr

D. 3.0 Torr

Figure 21. INFLUENCE OF PRESSURE, 1.0-3.0 TORR, 1" DIAMETER CATHODE



1" x 2-1/2" Cylindrical Cathode
150,000 ohm Series Resistors

Figure 22. SPECTRAL AND VOLTAGE-CURRENT RESPONSE CURVES (1" Diameter)

discharge, Figure 21. A similar series of curves was obtained with different series resistors.

It should be noted that the photomultiplier gain used was considerably greater in measuring the intensity of the nitrogen bandhead since it is considerably less intense than the hydrogen line when using room air at ca. 1% water-vapor concentration. The hollow cathode cell, Figure 23, designed for throughflow was used with the 1-inch cathodes. An unanticipated result of this anode-cathode configuration was the formation of an anode column along the axis of the holder behind the cathode, which almost filled the area between the anode and cathode in the 0.09- to 5-Torr range investigated. This may be eliminated if desirable by changing the anode placement relative to the cathode.

Since the large diameter cathodes seem to be effective in the low pressure region, and the small diameter is effective in lower pressures, a modification of a conical cathode was logical. Two cathodes with slightly different geometries were constructed, Figure 24. The main difference between the two was the diameter of the small opening. Cathode (1), Figure 24, was used first with the large cylinder anode in position A.

With 2000 volts EMF applied, the discharge lighted abruptly at ca. 0.8 Torr and continued to emit usable light even when the pressure exceeded 10 Torr. Still using the first cathode holder but using a small annular ring anode in position B, the above behavior was still observed at higher pressures, but the discharge was initiated at ca. 0.3 Torr.

From previous work with other geometries, it was known that increasing the size of this hole would give better characteristics at the low end of the pressure range with the sacrifice of output at the high end. The new cathode holder was prepared and tested with an annular ring anode. The discharge initiated at ca. 0.065 Torr and emitted usable light above 15 Torr.

These cathodes were prepared from tantalum foil. It was found, however, that the small part of the cathode oxidized badly after a comparatively short running time causing excessive fluctuations in the light output and electrical characteristics. This problem was solved by replacing the tantalum with platinum.

Figure 25 shows the relative outputs of the 6562.8-Å hydrogen line, and the 6553-Å nitrogen bandhead, as well as the electrical characteristics voltage, current and power, all versus pressure. The photomultiplier gain used for measuring the nitrogen bandhead was again considerably greater than that used for the hydrogen line. The air used was room air at ca.

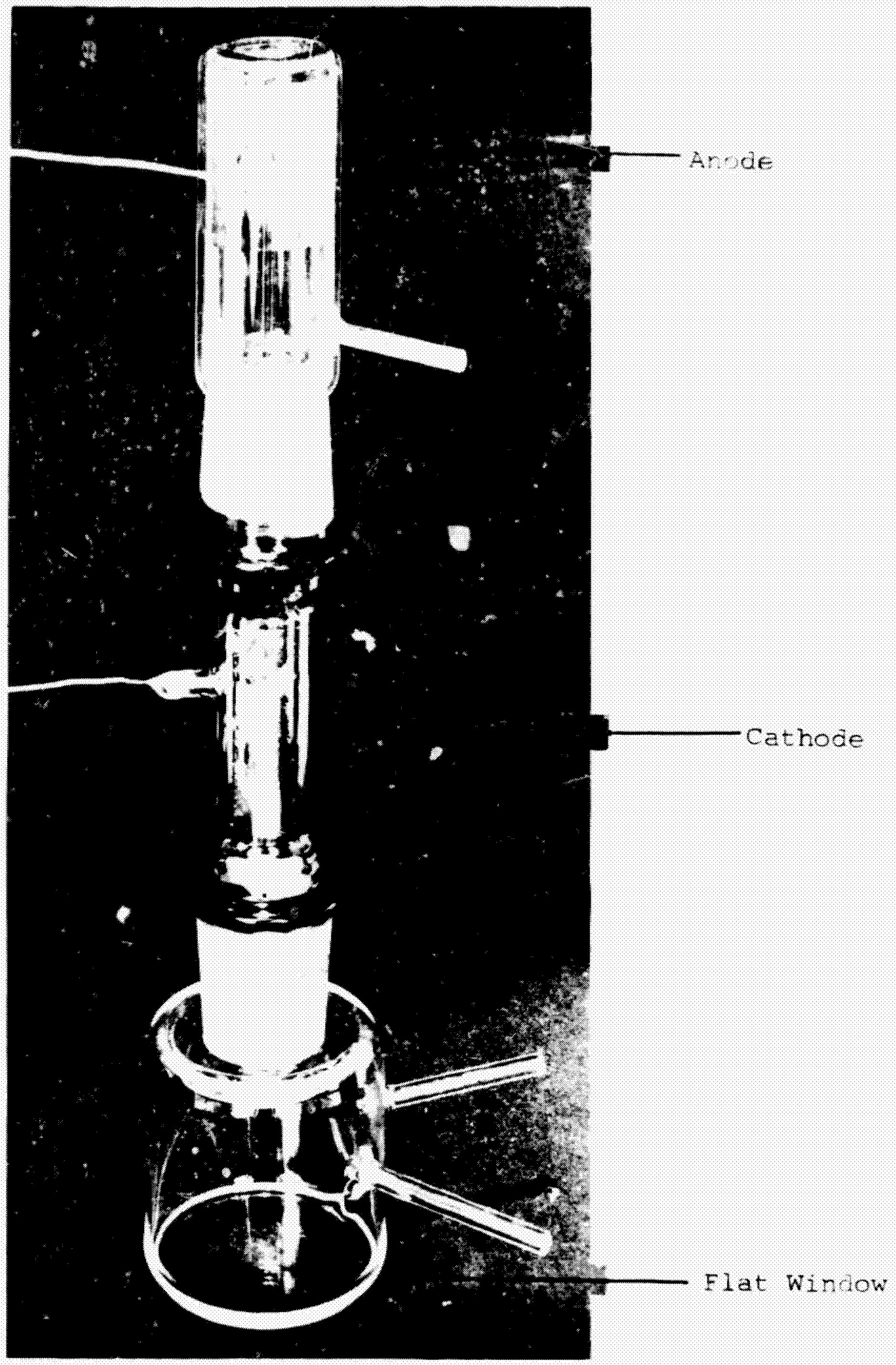
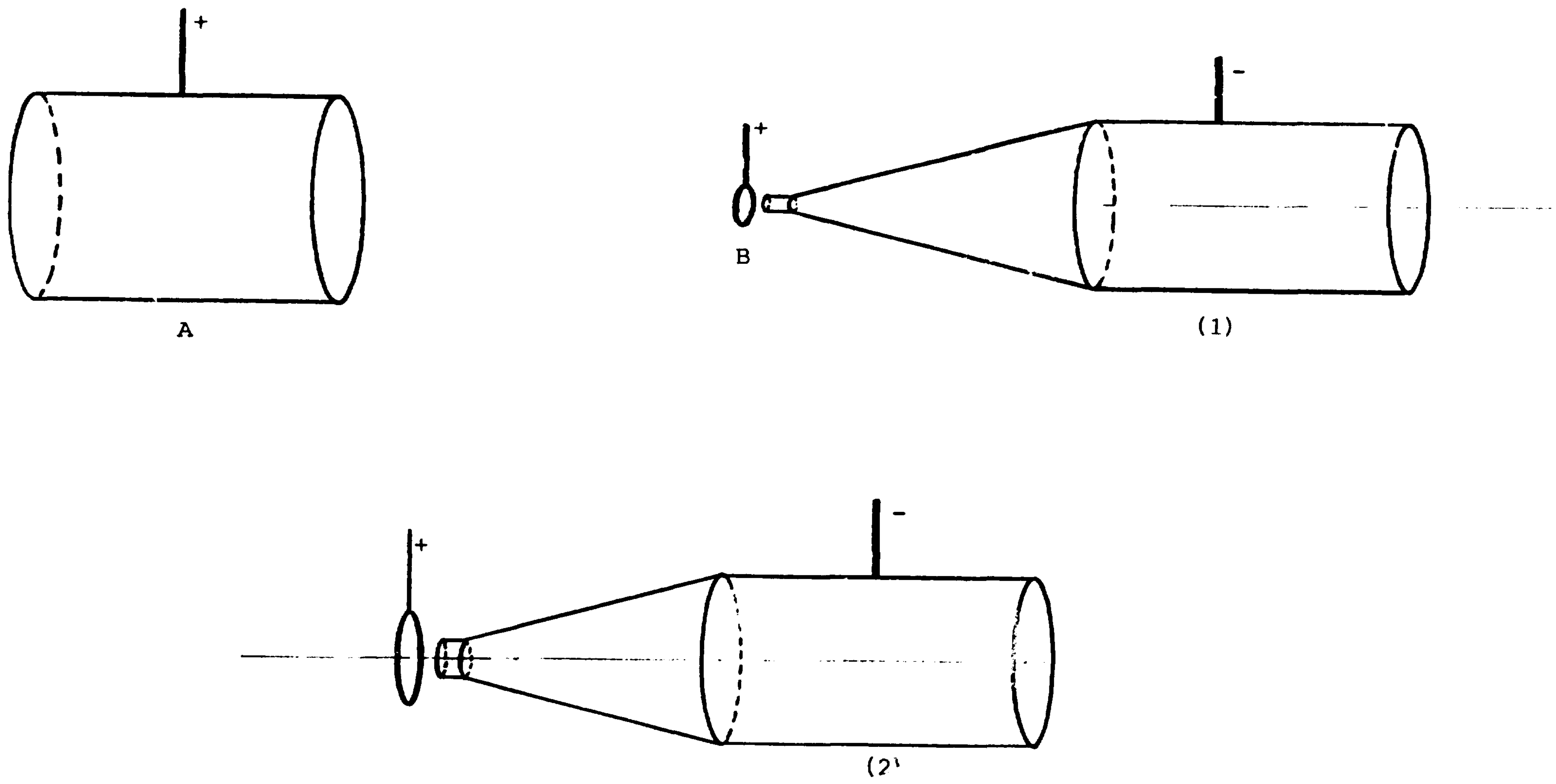


Figure 23. FLOW-THROUGH HOLLOW CATHODE CELL



Full Scale

Figure 24. CATHODE GEOMETRY AND ANODE PLACEMENT

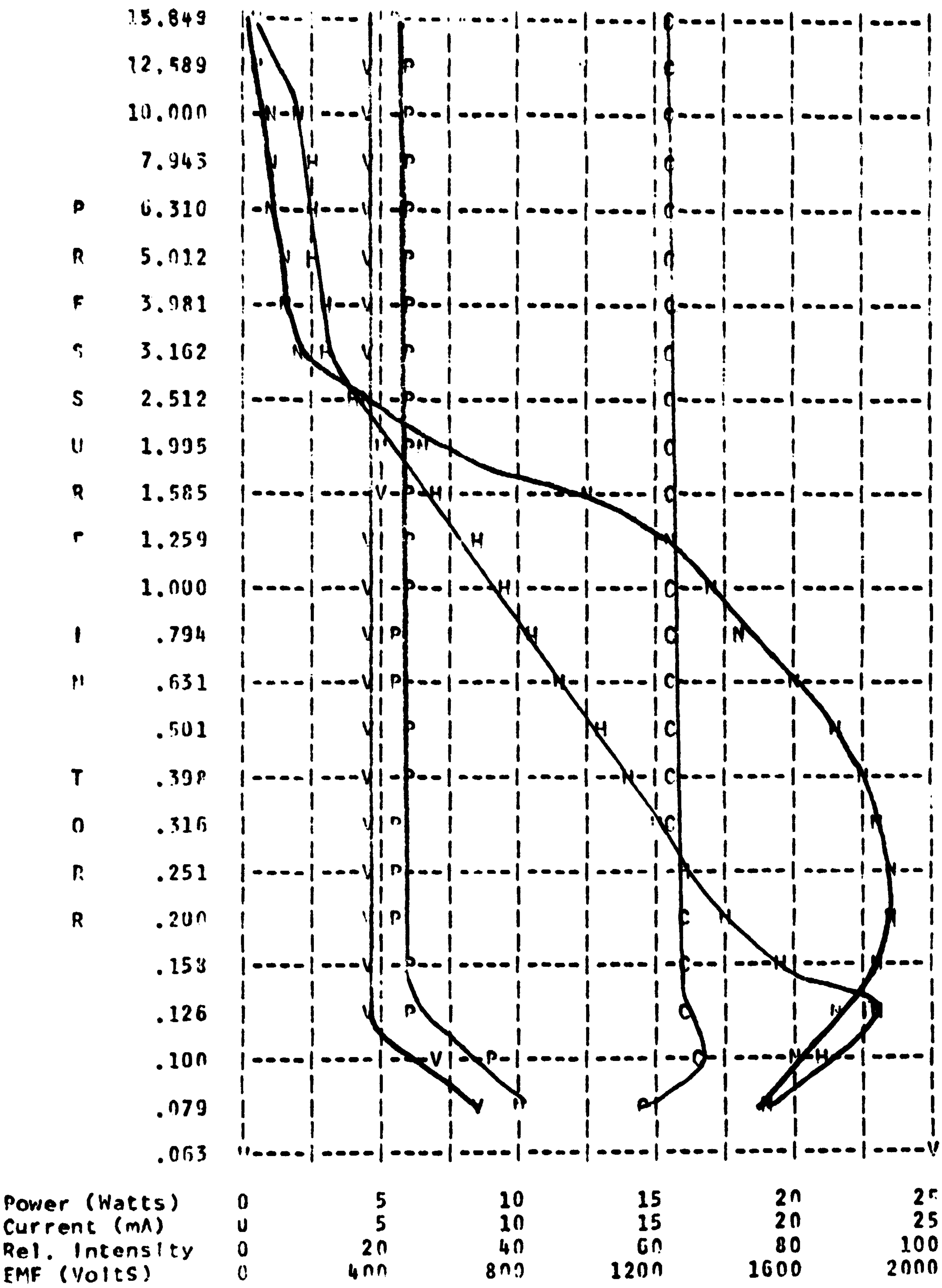


Figure 25. SPECTRAL AND VOLTAGE-CURRENT RESPONSE CURVES

1.2% absolute humidity. As with previous geometries, the rate of flow through the cathode did not seem to greatly influence output or electrical characteristics. The 6553-Å line in the nitrogen band structure was chosen after a study to determine which of the many lines in the vicinity varied most closely with the 6562.8-Å line on whose slope the hydrogen line appears.

B. Spectral Studies

The initial spectral studies with the tantalum cathode were performed with a Spex No. 1800 3/4-meter Czerny-Turner high aperture spectrograph. This unit had been modified such that a photomultiplier tube holder with a 200μ exit slit was used in place of the plate holder. As set up initially using a relatively wide entrance slit, 100μ, and the above exit slit, effective resolution was approximately 2 Å. With the nitrogen or air background in this region, a $\pm$1% precision in the 100 ppm range was not possible. An examination of this region's photographic plates from some previous work, on a high resolution instrument, showed this background structure, as illustrated in Figure 26, could be resolved much further. From Figure 26, prepared from dry hydrocarbon-free air, it would appear that more resolution was necessary. Figure 27 illustrates the spectrum of air containing water obtained with the spectrometer yielding an effective resolution of 0.6 Å. This tracing was encouraging and greater resolution should improve the line signal-to-background ratio. If this greater resolution should completely resolve the background from the hydrogen line, actually a doublet, then an excellent line-to-background ratio should develop. If complete resolution is not obtained, then the relative variation of a neighboring minima may be observed as a function of pressure and discharge current and the line-to-background over the pressure range can be established. There is no particular point of obtaining a resolution better than 0.1 Å because the separation of the hydrogen doublet is 0.124 Å.

For these reasons the hollow-cathode system was set up on a 3.4-meter Ebert mount spectrograph capable of 0.1 Å or less resolution.

An exit slit for the Jarrell-Ash spectrograph was constructed by scribing a 10μ groove in a vacuum-deposited aluminum film on glass. After installation, it was found that the spectograph was too slow to yield a usable signal-to-noise ratio from the photomultiplier. Since photographic plates offered an alternative means of studying this region, several sets were taken. Positive enlargements of the region of interest appear in Figures 28 and 29. Figure 28 was taken using room air at ca. 8000 ppm absolute humidity, and Figure 29 was made with dried air. The halation and graininess of the film, as well as

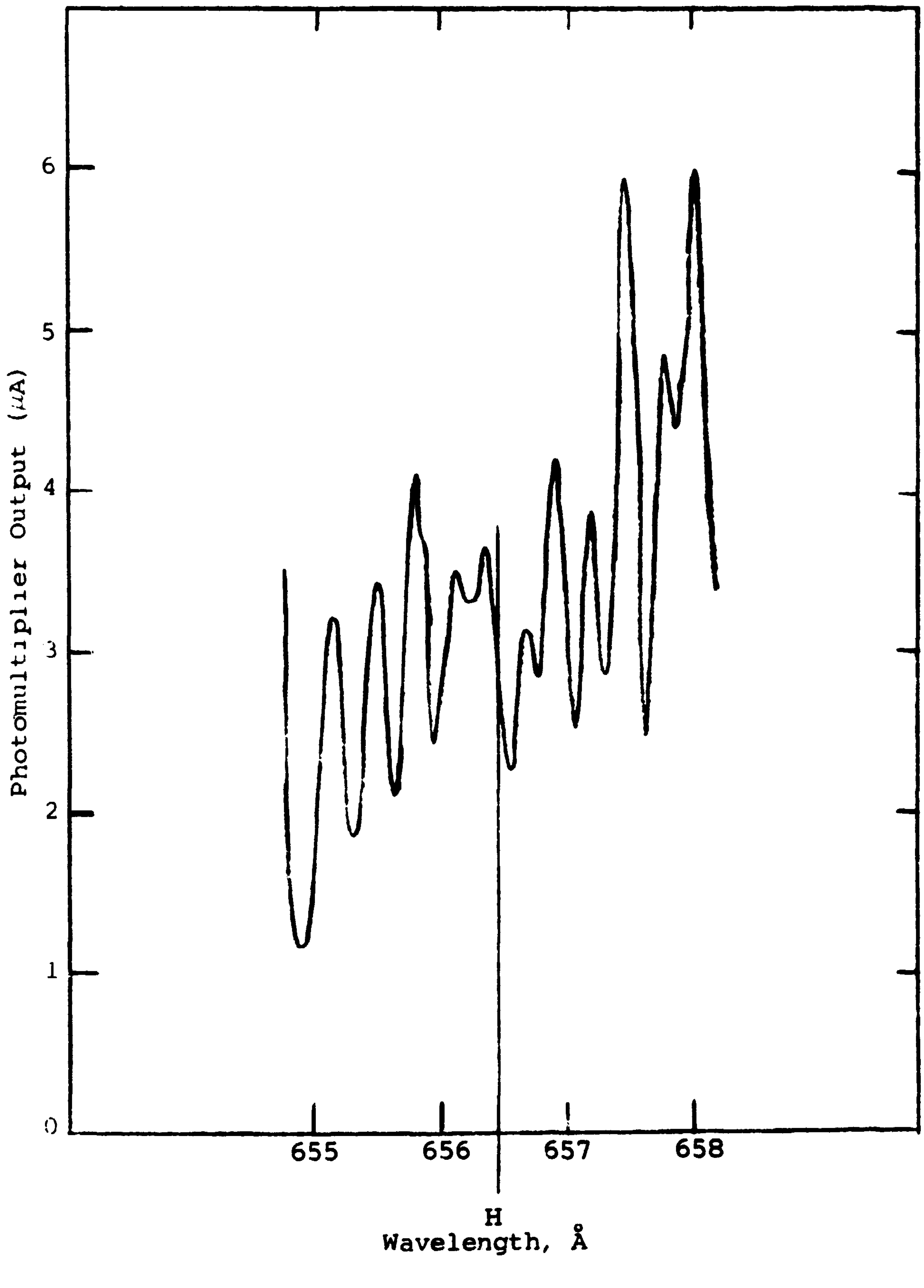


Figure 26. SPECTRUM SCAN OF DRY HYDROCARBON-FREE AIR (2 Å RESOLUTION)

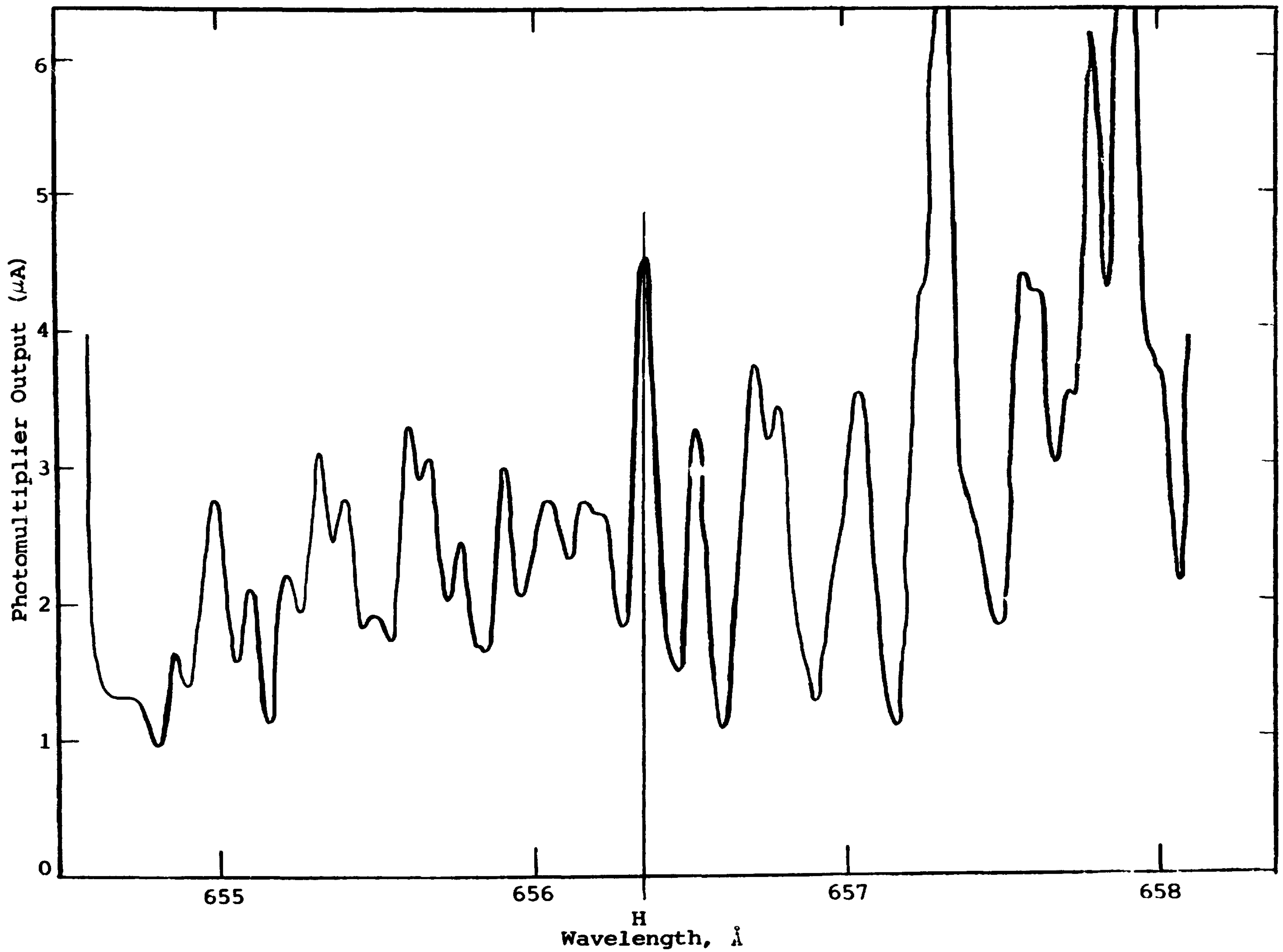


Figure 27. SPECTRUM SCAN OF AIR WITH 1% WATER VAPOR (0.6 Å RESOLUTION)

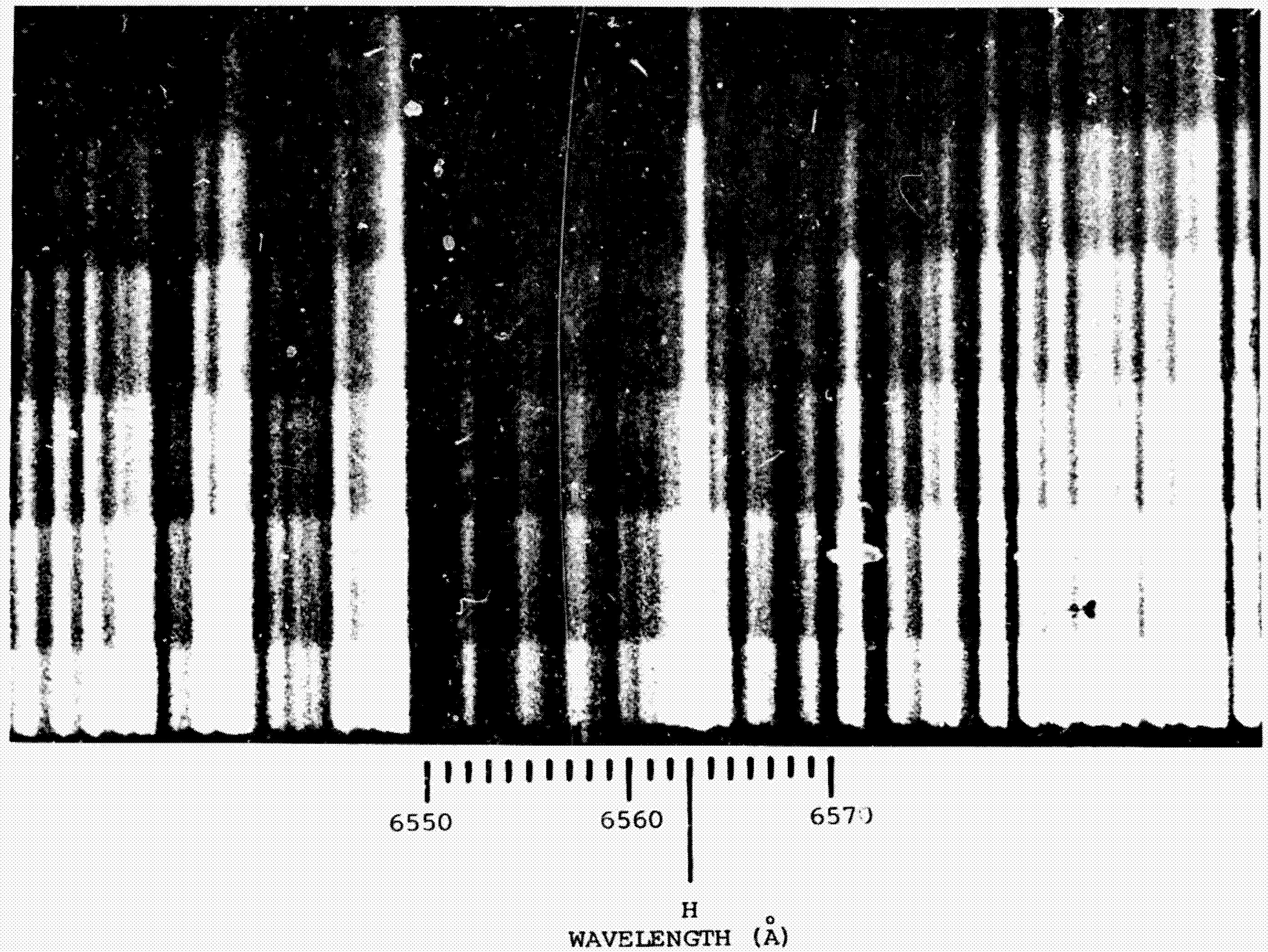


Figure 28. SPECTROGRAM ROOM AIR; 3.4-METER SPECTROGRAPH

a larger entrance slit limited the available resolution to the order of ca. 0.05 mm. The hydrogen line stands out in Figure 28. In Figure 29, the faint indication of a line at this wavelength is either a weak nitrogen or the air was not absolutely dry.

Later the photomultiplier tube and hollow cathode assembly were installed on a 1-meter Czerny-Turner scanning monochromator with adjustable exit and entrance slits. Actual resolution was between 0.1 and 0.2 Å. Scans were made in both first and second order for the 6563-Å region for dry nitrogen, dry air and room air using both platinum and gold cathode liners. Gold was used to replace platinum to see if the reactivity of hydrogen with the platinum-palladium metals was influencing the spectra. No differences were observed.

The spectral scans for dry nitrogen, dry air and room air are shown in Figures 30, 31, and 32, respetively. These scans show a nitrogen line at the hydrogen wavelength, Figure 30 and Figure 31, which varies in intensity with concentration and of such intensity that the influence of approximately 1% water vapor has little effect. We have been unable to find this line reported in the literature either as an atomic line or as part of a band. Photographs in the second order of this region show this to be a sharp line clearly visible through the more diffuse hydrogen line from the 1/2 to 1% water vapor range. Above these concentrations the spectral response for hydrogen becomes a function of concentration. The addition of helium in 50% or greater by volume reduces the nitrogen response and greatly enhances the hydrogen line intensity.

The higher resolution also showed a shorter periodicity of air spectrum than had been expected from other spectral scans. The output observed at the 6562-Å line appeared to be in keeping with this periodicity. The presence of this background line makes quantitative measurements of hydrogen concentration more difficult than planned since the light emitted by excited hydrogen atoms is added to this background. The intensity of the background emission is governed by the same parameters as is the hydrogen emission, namely, pressure, current, cathode temperature, etc. In the experimentation carried out to date, another line has not been found that varies in the same proportion as the line beneath the 6562-Å hydrogen line with changes in the above parameters.

Photographs of the 4861.3-Å hydrogen line and its spectral region at first looked promising in spite of the fact that this is a much weaker line than the 6562.8-Å line. However, at low concentration a background appeared that also made it difficult to measure low concentrations with a degree of precision.

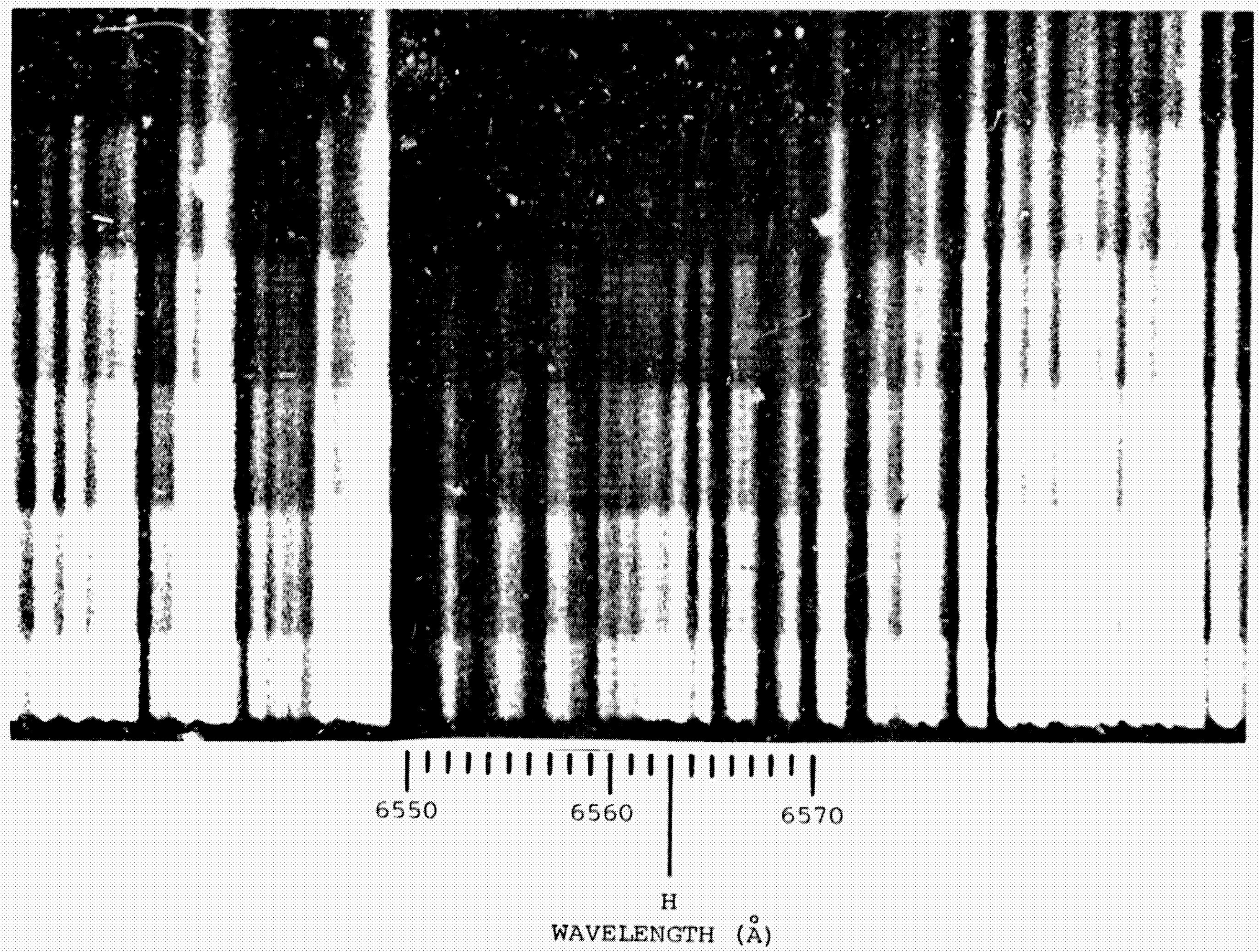


Figure 29. SPECTROGRAM DRY AIR; 3.4-METER SPECTROGRAPH

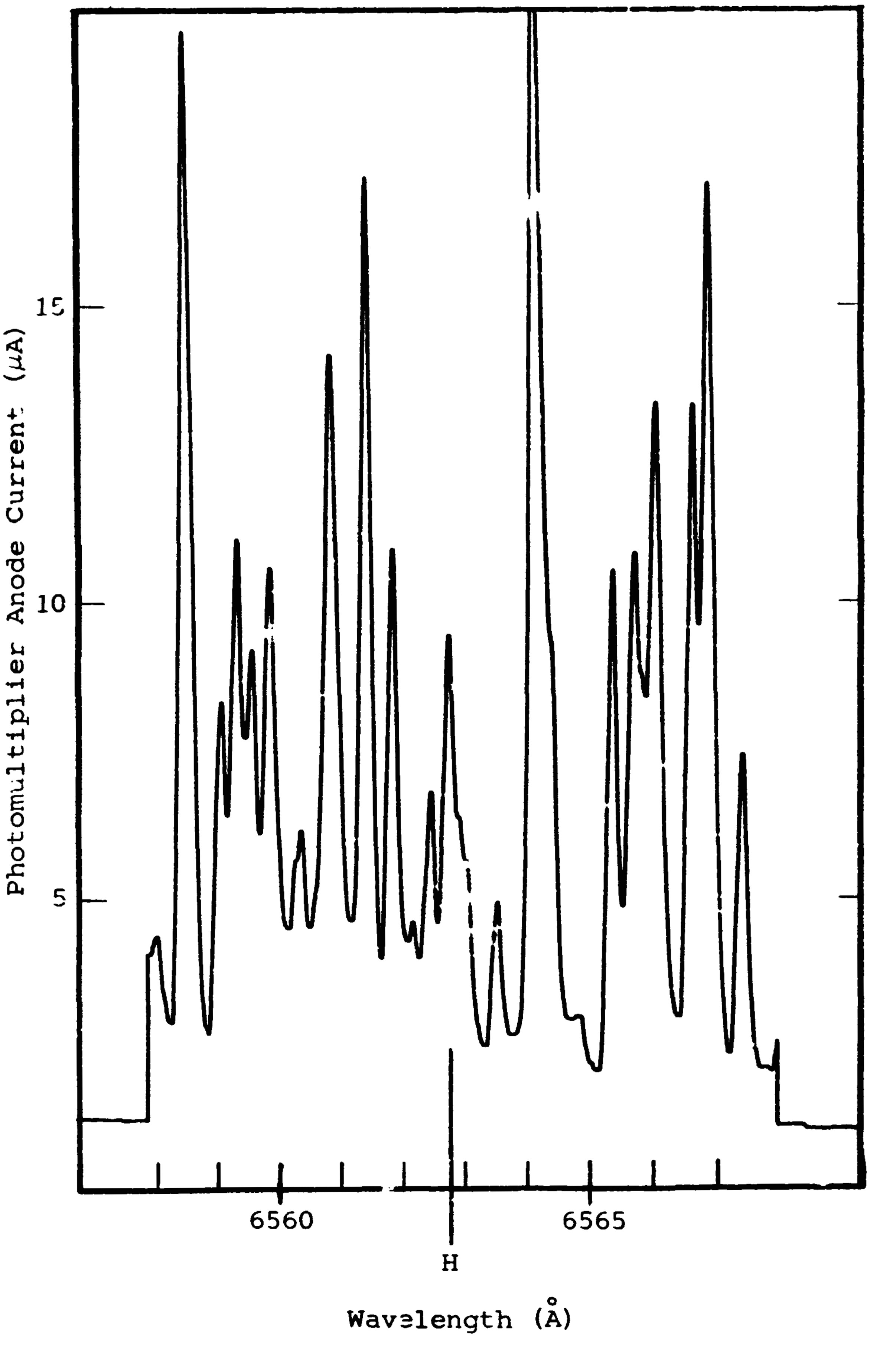


Figure 30. SPECTRAL SCAN OF DRY NITROGEN

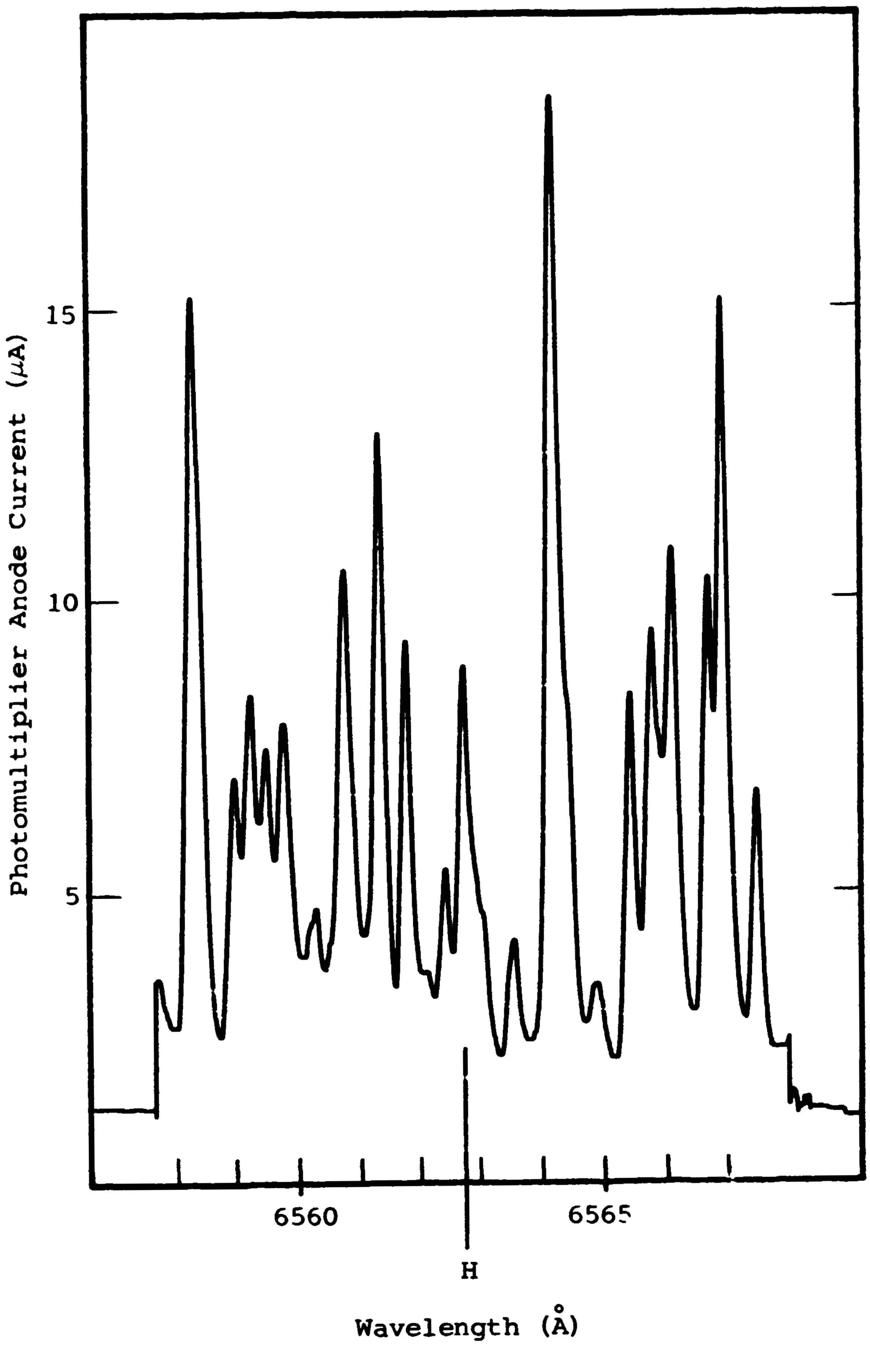


Figure 31. SPECTRAL SCAN OF DRY AIR

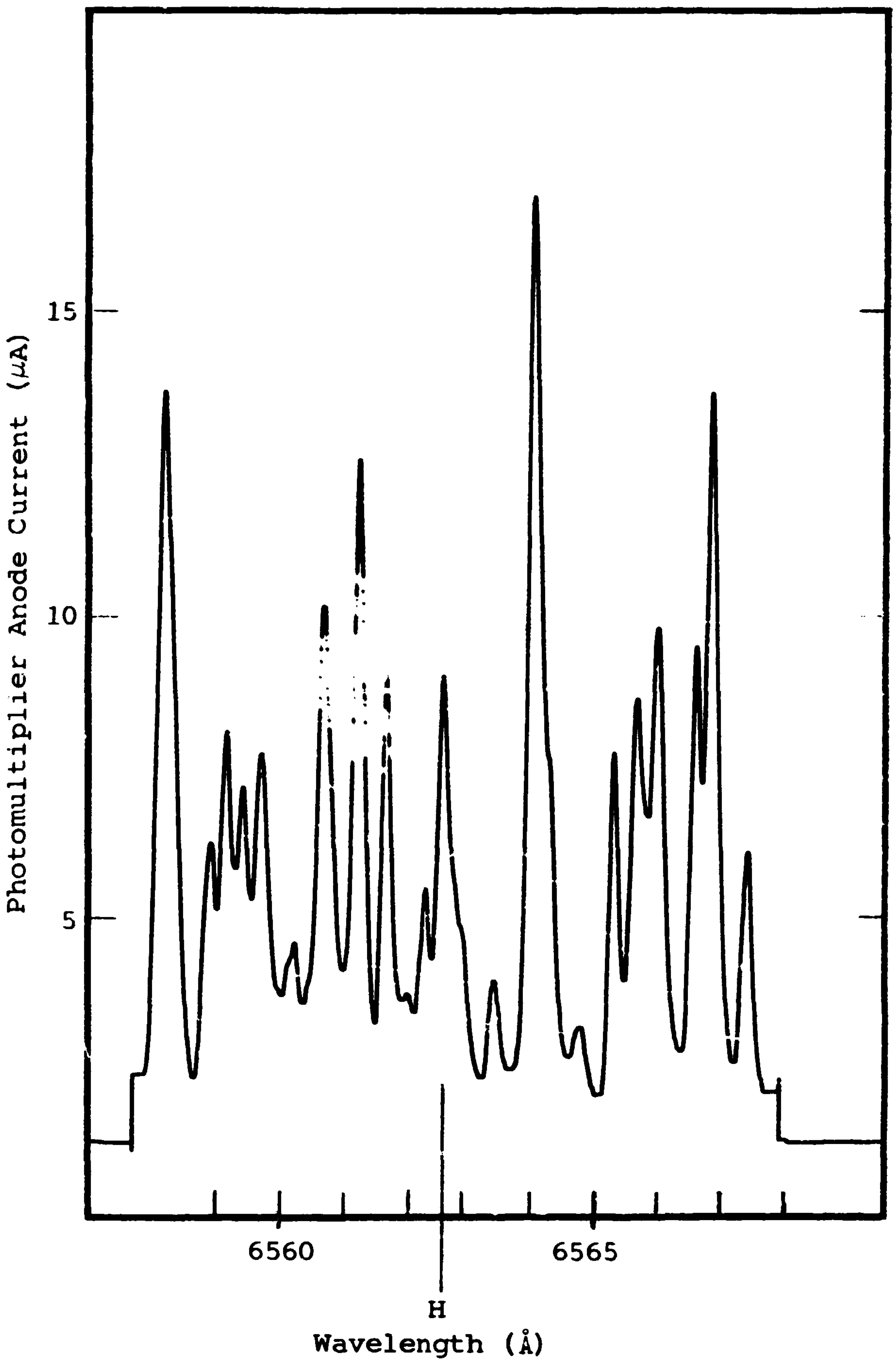


Figure 32. SPECTRAL SCAN OF ROOM AIR

IV. SUMMARY

The work described in this report consists of the design and construction of a gas handling system with gas purifier that is believed to be capable of delivering gases with less than 0.5 ppm hydrogen concentration; the design, construction and study of several types of cathode geometries, and the exploration of the spectral region near the 6562.8-Å hydrogen line. A hollow cathode geometry was found which operates over the pressure range of 0.1-10 Torr.

The study of the 6562.8-Å spectral region revealed that, under the conditions used in the experiments, nitrogen emission at 6562.8-Å region was much more intense than had been anticipated. Relatively weak band structures on each side of the 6563-Å hydrogen line were known to exist, but a line directly under the hydrogen line had not previously been observed. Since the light emission at the above wavelength is the sum of the nitrogen and hydrogen emission, the emission due to the hydrogen may be found by subtraction if the nitrogen intensity is known. It was observed that the uncertainty in measuring the emission due to the nitrogen emission was comparatively high. As a result, a calibration of hydrogen emission versus hydrogen concentration was not made. If it were possible to find a nitrogen spectral line or band which varied proportionately with that of 6562.8 Å, this uncertainty would be greatly decreased and such a calibration would be possible.